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ANALYSIS OF POROUS
ALKALINE Cd-ELECTRODES

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ANALYSIS OF POROUS

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The thesis consists of the following papers referred to by Roman numerals:

Analysis of porous alkaline Cd-electrodes

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I. Acidic high rate transients

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J. Appl. Electrochem., 4 (1974) 249-257

Analysis of porous alkaline Cd-electrodes

II. Potential recovery phenomena after a period of discharge

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J. Appl. DEPARTMENT OF CHEMICAL ENGINEERING

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Analysis of porous alkaline Cd-electrodes

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III. The application of Tafel plots in electrode design

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Per Selånger

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Analysis of porous alkaline Cd-electrodes

IV. Optimization of current efficiency

Per Selånger

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DISSERTATION

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ANALYSIS OF POROUS
ALKALINE CATION-EXCHANGERS

W. J. VAN DER KAM



DEPARTMENT OF CHEMICAL ENGINEERING
DUTCH INSTITUTE OF TECHNOLOGY

LEIDEN
THE NETHERLANDS

DISSERTATION
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1. INTRODUCTION

The market for electrochemical energy storers has been steadily growing the last 15 years. This expansion is expected to continue as one of the results during a growing number of nuclear-power-plant installations and of the expected electrical driven vehicles. Characteristic for electrochemical energy storers is the extensive use of expensive construction materials such as metals and metal compounds. In the competition with other application fields for construction materials and taking the limited global energy-resources into consideration (necessary for cheap metals), one can understand that it is an urgent task to find methods and principles of construction, which give more efficient utilization of the basic-materials.

To be able to develop more efficient methods, it is necessary to accumulate an extensive fund of knowledge of the working principles of electrodes and their limitations. Studies of accumulators have traditionally been on an empirical basis and closely related to commercial products. The accumulated fund of knowledge of different battery-systems, which has been collected during the last 80 years, is considerable and therefore difficult to survey. As most what we know is of an empirical nature, the necessary background material suitable for deep analysis is lacking.

The need for an analytical methodology to complete and render the knowledge more effective is therefore very obvious. As well as for technical reasons, it is also good research economy to use methods which lead to a more general analysis than with the empirical methods alone. As the methods which have been investigated here make great demands upon efficiency. A convenient working formula should be a combination of theoretical and experimental model-working.

1.1 The structure of a battery model

A battery model can be organized at different functional levels, which are shown in figure 1.

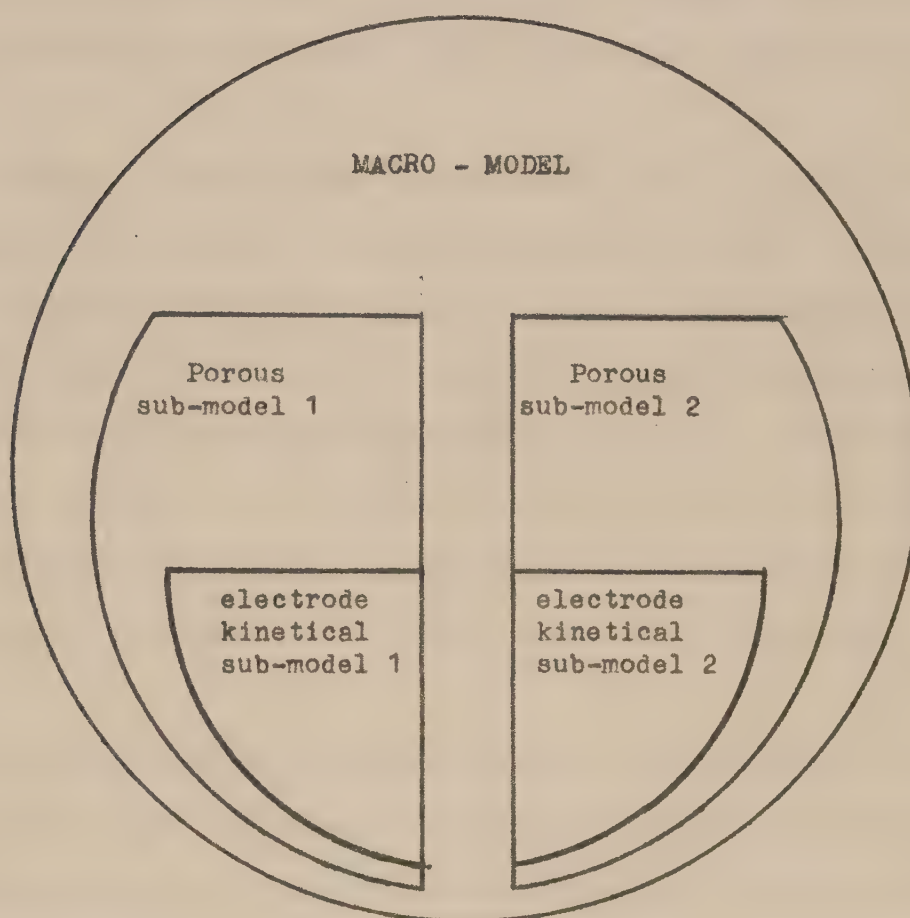


Figure 1

The concept of a macromodel covers the description of functions common to the two different electrodes in a cell, such as

Conductivity functions

Vessel design

Connections

Electrode design

Enclosures of the active electrode materials.

A macro-model will administrate precisely the kind of information which the traditional empirical analysis have been desired to deliver. A macro-model based on the mathematical methodology should therefore describe various polarisation processes and the distribution of current within the electrode geometries. A model with these properties is then suitable for optimization analysis, as the information is concentrated in the model. To obtain a macro-model with the desired properties it is necessary that the sub-models which constitute the macro-model fulfil their local function abilities.

Specific models to describe the properties of porous electrodes are needed and are represented here by the porous sub-models 1 and 2. A model for porous electrodes has to correctly reproduce the mass-transfer of the electrolyte constituents, describe the current distribution within the electrode and the structural changes which occur in the inside geometry during the discharge of an electrode. A model for a porous electrode has also to consider the effects on prestanda caused by the local geometry. The latter is connected with the type of enclosures for the active material.

Certain specific difficulties connected with the complex electrode structures appear in the study of the reaction kinetics in porous electrodes. Special kinetical models are in general required to support the porous models. This latter need is illustrated in Figure 1 in terms of the electrode kinetic-sub-models. Electrode kinetical sub-models on a mechanistic basis are in general not required for a practical porous electrode model. Correct mechanistic models are of course the best bases for a porous model and should be used if possible. The alternative to a strict mechanistic model is an experimental empirical model. The latter can made from correlations of, η - i , overpotential-current density data on logistic correlation functions corresponding to probable mechanistic routes.

Until now there has been no macro-models in the literature which is based on pure sub-models for two porous electrodes. Only one macro-model with dynamical properties based on semi-empirical sub-models is given [1]. The present stage of development has now reached the level of a functional description of porous electrodes and complete macro-models for accumulators will probably appear within the next decade.

1.2 The selection of porous cadmium-electrodes as a model object

A great number of models for porous electrodes have been presented in the literature from the last 15 years. Among this number there are only a few which have been analysed and compared with experimental background materials [2,3,4] (to be commented upon later). It has therefore been natural to direct this work towards a specific porous electrode system to gain methodical experience especially from the combination of theoretical and experimental work. The choice of alkaline cadmium-electrodes as the object of this study was based upon the following three points; The cadmium-electrode has been known for more than 70 years to be a very good and reproducible electrode and with a simple reaction product $\text{Cd}(\text{OH})_2$. The latter property is of great importance, as it is desirable to minimize the number of insecure factors in the study of a complex system. Metallic cadmium is expensive in comparison with many other battery metals, and as such it is a good object for economizing. The cadmium electrode has many good properties and it is reasonable to assume that the cadmium electrodes will still have a long market life. This latter quality is of importance, as the model-preparation works are rather extensive and the model-object should therefore in general have a good prognostic picture in order to be motivated as a model-object.

2. DYNAMICAL MODELS FOR FLOODED POROUS ELECTRODES

2.1 System description

Porous electrodes with flooded electrolytes are composed of two phases, a solid and a liquid phase. The dominant component in the solid phase is in general one of the reactants in the electrode reactions and constitutes together with added ingredients a porous matrix-phase with good electrical conductivity. The liquid phase also has the combined functional properties of having a conductivity and simultaneously providing a supply of reactants. The electrolyte phase is also the place to store sparingly soluble reaction products. The primary reactions take place in the inter-phase boundary between the two phases. The reactant limiting phase is in general the electrolyte phase. This limitation is explained by the fact that there is a higher concentration of reactants in the solid phase than in the liquid phase. This situation exists at ordinary electrode porosities (III). To obtain an electrode which functions efficiently it is of importance that the electrolyte-phase has a geometrical structure suited for mass-transfer of the electrolyte constituents. A functional model of a porous electrode should therefore describe the simultaneous effects from polarisation gained by mass-transfer, current conduction and precipitation of sparingly soluble reaction-products.

2.2 Earlier models

The first theoretical model for flooded porous electrodes developed in conjunction with experimental studies was produced in 1968 by R. Alkire [2]. The model system was composed of porous copper electrodes in a sulfuric-

acid electrolyte and with an exact defined pore-geometry. A "pseudo-steady-state"-model (from this point abbreviated as PSS-model) was developed for the anodic dissolution of copper. The model described the structural effects of the metal-dissolution. The studied reaction system had very limited value from the battery technological point of view, as the anodic dissolution of copper leads to an enlarged reaction-surface. The reverse situation is the case for the most useful battery-electrode systems, where the reaction surface decreases throughout precipitation of reaction products.

A more applicable model for accumulator electrodes was developed by Dunning, Bennion and Newman [3]. A PSS-model for sparingly soluble reaction products was used in the analysis of porous electrodes in the Ag/AgCl and Cd/Cd(OH)₂ systems. PSS-models have a limited capability, as there is no PSS-state over a certain current-load [5]. In practice the PSS-models are not useful in the analysis of high-rate transients.

Simonsson [4] presented a model for the PbO₂ electrode in the lead-acid system. The precipitation of reaction products was simulated as was observed as a continuous plugging front through the electrodes. The transport model used was simplified and was thus derived from the laws which are valid only for diluted electrolytes. The model, showed, however, a correlation between the experimental current-distributions and those which were calculated with the model.

3. A MODEL FOR POROUS ALKALINE CADMIUM-ELECTRODES

The aim of the studies related here is to find a methodology for evaluation of porous electrode-materials. The determination of the parameters and constants which are parts of the mathematical system-description is of particular interest. The determination of parameters forms the basis for further applications of the model in connection with macro-model preparations. To be able to determine the intended constants and parameters it is important that the polarisation affecting processes will be correctly interpreted. For an appropriate process identification a number of experimental activities are required of which some steps already have been carried out and are reported in the works mentioned previously. Table 1 shows the experimental works which have been compared with dynamical mathematical models.

Table 1

Dynamical models for porous electrodes with experimental verifications of predicted behaviours.

subject	methods and models	system and investigators
current distribution distribution of the active material	Stacks of thin electrodes were analysed individually and with respect to their positions. Static-state model.	/6, / Gagnon and Austin Ag/Ag ₂ O in alkali
	Sintered powder electrodes. Section analyses of electrodes at different intervals of time and load conditions.	/7/ Bro and Kang Cd/Cd(OH) ₂
	Micro-probe analysis of electrode cross-sections. A static-state model was used with known concentration profiles.	/8/ Simonsson PbO ₂ in sulfuric acid
	Charged electrodes were sectioned to obtain initial state distributions. Permeability analysis of discharged electrodes.	/9/ Selånger Cd/Cd(OH) ₂
concentration profiles	Titration analysis of sectioned electrodes	/10/ Simonsson PbO ₂ in sulfuric acid
polarisation transients	PSS-model based on data from Bro and Kang	/3/ Dunning, Bennion and Newman. Cd/Cd(OH) ₂
	Model based on solutions of PDE-equations.	/4/ Simonsson
		/9/ Selånger
	Diffusion potentials in the current free state after a period of discharge.	/11/ Selånger

3.1 The current distribution

The various models listed in table 1 fulfil the conditions for the description of the internal current distributions in flat open porous electrodes. All the models are based upon the assumption of the electrode material as a pseudo-homogeneous medium derived from a super-position of two continuous phases representing the solid matrix phase and the pore-electrolyte phase. The models predict a non-uniform current-distribution with the greatest reaction-currents within the pore-mouth region which is the case for electrodes with good conducting solid matrices. The effect of non-uniform current-distribution grows with the resistivity of the electrolyte, the reaction surface activity and the total current load.

Minor deviations relative to the results with the earlier models were obtained with the model used in this work (I). At large current-densities a load dependent electrode activity was observed, which is defined as $i_0 S(1-\epsilon)(1-u)$. Where $u = \frac{k_{bl}}{\epsilon^{0.5}} \cdot \frac{\partial i}{\partial x}$, expresses the current load-dependency. The effect of u is that the current-distribution tends to be more uniform than that obtained by other models as the result of the lowered reaction activity. In the publication (I) u was assumed to account for an increasing number of deactivated pores caused by an insufficient mass transfer ability in the smallest pores. The relation $1/\epsilon^{0.5}$ is empirical and is not resolved in this work to the deterministic level.

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3.2 Concentration profiles

The mass-transport mechanisms represented in model (I) are diffusion and convection. Transport by ionic-migration in the electric field is negligible. Here the convection is the effect of the displacement of electrolyte as a result of the precipitation of a sparingly soluble reaction product. The reaction product has a greater mole-volume than the reactants and the convection obtained results in a loss of electrolyte within the electrodes.

No direct measurements of the electrolyte concentration in specific electrode co-ordinates were made. The information about the variations in concentration has been followed indirectly and by simulations with a theoretical mass-transfer model (II). Calculated concentration profiles from current active states were used as initial states in the simulation of the potential recovery transients in a current free state after the discharges. This latter method is a useful complement to the study of the current activated state, as it gives an opportunity to test the validity of the diffusion term in the general model (I). Recovery transients do not only reflect the concentration profiles, they also give a response for the porosity distribution patterns. The results are surprisingly good with respect to the numerical insensitivity which is the case with an indirect method. The logarithmical relation between concentrations and the diffusion potential according to the Nernst's equation explains some of the insensitive numerical properties.

3.3 Structural changes

The active material in charged electrodes was investigated using a sectionalizing technique (I). The distribution of valences for cadmium was carried out to find out the fractions of the metallic state and the unconverted oxide. There were grounds to analyse the charge-distribution, as the electrodes were formed by reduction of the oxide directly in the electrode-holders. Electrodes with small porosities $\epsilon < 0.5$ had a larger frequency of non-uniform charged initial profiles than electrodes with higher porosities. The degree of charge was in general growing from the pore-mouth side towards the collector. The degree of charging is represented in model (I) with a density function g . The estimations on the parameter group $i_0 S$ with an assumed uniform charge-distribution initially gave poor results, which gave extra motivation for the section analysis.

The addition of an extra variable u , which has been discussed previously became a necessary measure from the estimation trials on $i_0 S$. The experimental electrode transients were analysed in order to find $i_0 S$ values. A group of apparently unsystematic $i_0 S$ values were obtained. In a closer analysis it was possible to show that $i_0 S$ was dependent on the load conditions and on the electrode porosity.

The expression $i_0 S (1-\epsilon)(1-u)$ took form and $i_0 S$ was from this point converted to a constant from the apparently undetermined variable status. A closer least-square analysis gave

$$u = k_{bl} \frac{1}{\epsilon^{0.5}} \frac{di}{dx}$$

with acceptable precision, 5 % in $i_0 S$. The latter formula expresses the need for a more extensive model, which take care of the load-dependence in a less empirical way.

The expression for reaction activity, $i_0 S(1-\epsilon)(1-u)$, is not applicable within the whole interval of porosity, but it covers the interval of technological interest. At porosities lower than 0.4, the deviations were great between the given formula and reality. Dramatically lowered activities occurred with decreasing porosities below $\epsilon = 0.4$. An ineffective inter-connected electrolyte space produces decreased activity, which is caused by the close-packing properties of the solid-phase. The accessible reaction surface is assumed to be drastically reduced in the porosity interval where the small pores are responsible for the electrolyte space inter-connections. Different pore-structures emanating from various particle forms and sizes give different properties of close-packing and it can be expected that different electrode preparations will give other critical porosity values than obtained here. The critical porosity has been defined as the porosity where the electrode-activity is decreasing to a zero-value. The actual electrode material gave a well defined critical value, $\epsilon = 0.34$.

The precipitation of the sparingly soluble reaction product $\text{Cd}(\text{OH})_2$ leads to porosity changes during the discharge process. According to principles described earlier a reduced porosity is obtained as a result of the precipitation. From the interpretation made of the experimental test material it was concluded that blockage of electrodes occurs predominantly for low current-densities and at low-porosity electrodes. High rate discharges on the other hand are pure diffusion controlled at all porosities. The point of change between the two controlling processes was obtained within the interval of 100-200 mA/cm^2 and is dependent on the porosity of the charged electrodes.

A special diagram (III) was developed in order to visualize the effects on the porosity variable from the precipitation of the sparingly soluble reaction

product. A charge-porosity diagram shows the relation between charge - capacity and porosity and is based on the differences in mole-volumes between solid reactants and reaction products. The effect of inert support materials is also represented in the diagram. The diagram can be used as a guide in the prediction of pore-blockage properties which are of interest in the design of an active material.

3.4 Polarisation transients

Few comparisons of theoretical and experimental polarisation transients are made in the literature. Dunning, Bennion and Newman [3] calculated transients for the system $\text{Cd}/\text{Cd}(\text{OH})_2$ based on data given by Bro and Kang. Differences between the model and the experiment were reported for the largest current densities. The model predicted a lower polarisation level than the experimental level. This difference can be explained in terms of the load-dependent reaction activity, in the model developed in this work (I).

The greatest difficulty to overcome in the prediction of an experimental transient with a model, is that of predicting a whole polarisation curve until the electrodes polarises infinitely. At high rates the pure transport theory is not good enough to explain the final parts of the transients. The pure transport theory gives transients which are too long. A surface-blockage function is needed and is written in terms of a surface-density function g

$$g = g_0(1-y^p)$$

The variable g_0 is the initial density of available reaction-surface activity, y is the extent of reaction and p is a structure parameter according to Dunning et.al. [3].

In the electrode material examined p was determined to 0.80. The need for a parameter p and the load dependent reaction surface activity with the empirical variable u discussed earlier, points out the necessity for an extended theory on porous electrodes to obtain a more deterministic model.

3.5 Determination of model parameters

The parameter represented in the model (I) is the following: α_a , α_c , $i_0 S$, ϵ , p and k_{bl} . The charge-transfer co-efficients are known for some electrode reactions and in cases where they are not known a special kinetical investigation is necessary with methods treated in standard textbooks 12. In the determination of $i_0 S(1-\epsilon)(1-u)$ initial time data is to be collected from polarisation transients, where the concentration polarisation influence is lowest.

With known electrode porosities one can determine the apparent reaction activity group $(i_0 S)_{app}$ from different load conditions with least-square procedures. The determination of porosity is described in work (I). The apparent values $(i_0 S)_{app}$, are then to be analysed with regard to the load dependence to obtain a suitable formula representation for the variable u . If one wants to obtain u in the form of

$$u = k_{bl} \frac{1}{\epsilon^{0.5}} \frac{di}{dx}$$

k_{bl} is to be determined with the least-square analysis. The parameter p is determined by least square analysis on the length of discharge-curves.

The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function, and its value is determined by the initial condition $f(0) = 1$.

2. The second part of the paper

In the second part of the paper, we consider the problem of finding the maximum value of the function $f(x)$ on the interval $[0, 1]$. It is shown that the maximum value is attained at $x = 0$ and is equal to 1. This result is obtained by using the properties of the function $f(x)$ and the fact that $f(x)$ is a constant function.

The third part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function, and its value is determined by the initial condition $f(0) = 1$.

$$\frac{1}{x} = \frac{1}{x}$$

The fourth part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function, and its value is determined by the initial condition $f(0) = 1$.

4. OPTIMIZATION

The developed model (I) for porous Cd-electrodes can be used in the characterization of porous active materials and one of the aspects of this characterization is an optimization analysis as a means of determining a material's loading properties. The object of this optimization analysis is to determine the design which gives the best utilization of the active material for various formulated problems. Here the best electrode design is selected from the best combination of electrode-thickness and porosity. Three different problems were treated in work (IV) and with the following formulations:

Problem I

The electrode capacity per square centimeter of electrode area which gives the best utilization of the active material for a given current load and final polarisation is to be determined.

Problem II

The smallest electrode capacity necessary to fulfil a given current load and final polarisation conditions in a given interval of time is to be found.

Problem III

The electrode capacity per square centimeter of electrode area which gives the best utilization of the active material is to be determined with respect to the utilization of the electrode space.

Problem I is the least restrictive formulated problem of these three problems, and is strictly a current efficiency problem. Problem II which has a final time condition to meet, is characteristic of many high rate applications. Problem I is to be solved with a maximum performance strategy, and problem II with a minimum strategy. Maximum utilization of the charge capacity and the minimum amount of active material are the index of performance respectively.

The conclusion from problems I and II is that a manufacturer of batteries has to make a choice between the goals of the highest efficiency and the least amount of active material to obtain the best electrodes.

The general results from the outcome of the problems are the following relationships for optimal solutions,

$$Q_I^+ > Q_{II}^+$$

and

$$\eta_I^+ > \eta_{II}^+$$

where Q^+ are the optimal capacities and η^+ the optimal current-efficiencies for problems I respectively II. The relationships show that the higher efficiency gained in problem I is obtained through using a greater amount of active material than used in problem II which produces a lower efficiency. To obtain the best electrodes a manufacturer has obviously to make a choice between goals of high amount efficiency and the least amount of active material or a compromise with weighted combination of both.

Problem III is to some extent analogous to problem I and the difference between I and III is that the current efficiency in III is obtained with regard to the utilization of the electrode space.

The procedures applied in (IV) and in conjunction with the model building technique presented in (I) will be powerful tools for the future in the continuous work of collecting and characterizing new and old active materials. The numerical model technique will make this work efficient because the information is stored in an efficient way, within the model.

This latter property is of importance when the time comes to analyse the ensemble of characterized active materials, the ultimate aim being to find the horizon of prestanda for porous electrodes. The horizon of prestanda is defined here as the ultimate limit in current efficiency for selected loading conditions.

It is of great importance to establish the horizon of prestanda for an electrode system as it defines the various goals for developments in the manufacturers' laboratories. The gap between the horizon of prestanda and the standard of technical electrodes together with economical conditions define the various potentials in the development of electrodes in the future.

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Per Selånger

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7 ERROR CORRECTIONS IN THE PRINTED MATTER

Paper (I)

page	text	column	line	Corrections
251	right		1 (under fig.1)	text to be added is "in the full charged state. A minor part of the" solid phase...
252	left		1	text to be deleted is "in the full charged state. A minor part of the" ...
252	left		10	$\text{Cu}(\text{OH})_2$ is to be changed to $\text{Cd}(\text{OH})_2$
252	right		equation (4)	the right member should be $v \frac{\partial c}{\partial x} + c \frac{\partial v}{\partial x}$
253	left		equation (8)	derivatives in the right member are partial- derivatives $D_{\text{eff}} \left(1 - \frac{d \ln c_w}{d \ln c} \right) \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - c \frac{\partial v}{\partial x} + \frac{v_r}{n^w} \frac{\partial i_2}{\partial x}$
253	right		equation (12)	the correct equation is $v = \frac{\int_0^t \frac{di}{dx} dt}{0}$
254	left		20	equations (19) are to be introduced as "At $x = 0$, $i_2 = \frac{I}{\epsilon}$, $c = c_0$ the pore-mouth conditions (19)".

Paper (II)

260	left		equation	correct equations is $\frac{\partial c}{\partial t} = D_{\text{eff}} \left(1 - \frac{d \ln c_w}{d \ln c} \right) \frac{\partial^2 c}{\partial x^2}$
261	right		21	"The dotted line h shows" ... h is to be deleted.

Paper (III)

264	left		3	corrected equation is $\epsilon_R = \frac{1}{1 + \frac{c^M_{\text{Cd}}}{2\rho_{\text{Cd}}}} = \frac{1}{1 + \frac{5 \cdot 10^{-3} \cdot 112.4}{2 \cdot 8.64}} = 0.97 \quad (3)$
265	right		equations (6) and (9)	$\text{Cd}(\text{OH})^2$ has to be changed to $\text{Cd}(\text{OH})_2$

Analysis of porous alkaline Cd-electrodes.

I. Anodic high rate transients

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Galvanostatic anodic high-rate transients in porous Cd-electrodes are analysed. A one-dimensional electrode model is developed. The model includes effects of variation in electrolyte composition and reaction surface activity. Overpotential transients are computed and compared with experimental transients. Failure in low porosity electrodes with great surface activity is in general caused by the blockage of pores at low rates. At high rates the discharge depth is limited by pure mass-transfer limitations. The reaction activity group i_0S is estimated from the experimental electrodes in conjunction with the model. Transition from pore blockage to pure mass-transfer limitations occurs between 100 and 200 mA cm⁻² for a medium porosity of 0.60.

Nomenclature

Symbols

c	electrolyte concentration, KOH, mol cm ⁻³
c_w	solvent concentration, water, mol cm ⁻³
D	diffusion coefficient, cm ² s ⁻¹
f	equivalents of extender on a Cd basis
F	the Faraday equivalent, 96487 As per mol equiv.
g	a density function for accessible surface activity; also the gravity constant, cm s ⁻²
i	current density, A cm ⁻²
I	current density, electrode load, A cm ⁻²
k_{bl}	blockage constant for small pores, cm ³ A ⁻¹
l	electrode thickness, cm
M	mole weights
Q	charge density, A min cm ⁻³
R	universal gas constant 8.3143 J K ⁻¹ mol ⁻¹
S	surface activity, cm ² per cm ³
t	time, s
i_+^0	the transference number of the cation in the binary electrolyte with respect to the velocity of solvent.
v	convective velocity, cm s ⁻¹
$\bar{V}$	mole volume, cm ³ mol ⁻¹

x	location co-ordinate inside the electrode, cm
y	reaction extent related to total amount cadmium
z_+	the charge number of the cation in the binary electrolyte

Greek letters

α	charge transfer coefficients $\beta F/RT$ and $(1-\beta)F/RT$, V ⁻¹
β	symmetry factor for charge transfer, = 0.5 was applied
ε	porosity
ρ	density, g cm ⁻³
κ	conductivity, ohm ⁻¹ cm ⁻¹ and permeability, cm ²
η	overpotential, V
μ	viscosity g cm ⁻¹ s ⁻¹
ν	stoichiometric coefficient
ν_+	number of cations into which a molecule of electrolyte dissociates

Subscripts

a	anodic
c	cathodic

d	diffusion
eff	effective
i	species i
o	initial time distributions along the electrode co-ordinate x
p	permeability
r	electrolyte reactant
t	charge transfer
1	solid phase
2	pore-electrolyte phase

1. Introduction

In this work a combination of experimental and theoretical work is carried out in order to gain experience from mathematical models as a means of analysing high rate electrodes.

The chief high-rate application of alkaline storage batteries is found in various engine cranking operations. A common property of batteries in heavy duty applications is the poor efficiency in the utilization of the active electrode material [1]. The materials used in electrodes are usually very expensive and this gives a rational motivation for an analysis to acquire a better background for making better electrodes in the future. The high-rate processes present a very complex problem and a performance analysis in general, should describe the overpotential transients at various load conditions. The load levels studied here are in the interval of 100–200 mA cm⁻² and these levels draw attention to the important problem of mass transfer and current distributions within the porous electrodes. In the complete analysis the effects associated with structural changes arising from the precipitation of a solid product Cd(OH)₂ are also to be considered.

There have so far been very few integrated analyses [2–3] which reflect the usefulness of taking advantage of theoretical models in the analysis of experimental electrode transients. The analysis presented in this work is a method for the determination of parameters which are of importance for the simulation of commercial electrode systems and for their optimization.

2. Experimental

2.1. Preparation

Electrodes were prepared from dry mixtures of CdO and Fe₂O₃. The proportions were on a weight basis in the ratio 90:10. The mixtures were pressed into an electrode holder of plexi-resin which defined a one-dimensional geometry, as the inside walls were electrically isolated. The electrode backing was made of machined rods of Ni metal. Through variation of the formation pressure it was possible to obtain different porosities. In the preparation of highly porous electrodes it was necessary to add finely divided KOH to the mixture to obtain a form-strength. The KOH was then leached out after a pre-reduction in a saturated KOH solution. The maximum porosity obtained by these methods was 0.85 and the minimum was 0.33. The electrode thickness varied from 0.7 to 2 mm. The electrode diameter was 10 mm.

During the formation cycles it was observed that the behaviour (i.e. reproducible discharges) of the electrodes became constant after 4 to 5 cycles. A pre-reduction for 48 h at 1 mA cm⁻² was then followed by repetitive discharges and charges with the same current density for periods of 12 h. After a final conditioning, 24–28 h, the electrodes were ready for measurements at reproducible equilibrium potentials against a Hg|HgO cell in equal KOH concentration.

2.2. Measurements

All potential measurements were under galvanostatic conditions. The bulk electrolyte was stirred to eliminate the concentration potential error from the bulkside gradient. The overpotential at the working electrode was measured with a conventional Luggin-capillary connected to a reference-cell of Hg|HgO in the same electrolyte. The polarizations were registered on a paper strip-recorder after compensation for the equilibrium potential.

The temperature during the various runs was 22±0.5°C and the electrolyte concentration varied between 4.5 and 5 M. The average porosities were determined by a volumetric neutralization titration procedure, combined with

electrode thickness measurements with a micro-meter screw gauge. The mechanical volume was calculated from thickness data and the constructed electrode area. The electrolyte inside the electrodes was leached out with pure water. The leaching was repeated four times with pure water. The leached liquor was titrated with hydrochloric acid and related to the electrolyte volume inside the electrodes. The adherent electrolyte on the outer surface, was quickly washed away with water and thus excluded from the titration volume.

The charge distribution inside the electrodes was determined from microtome sectioned slices by chemical analysis. Sections with a thickness of 50 μm were analysed by the polarographic method for determination of the valence state distribution in the cadmium phase [4]. Only measurements of relative values between the metallic and the ionic states gave reliable results. The failure in the total value analysis was caused by the poor electrode strength, which produced only fractions of the sections under the microtome knife. The electrodes were embedded in a thin body of epoxy-resin and sliced under air-excluded conditions.

BET surface measurements were performed for some of the charged electrodes and for the ground materials. The cadmium oxide used was 5.0 $\text{m}^2 \text{g}^{-1}$ and the ferric oxide was 8.8 $\text{m}^2 \text{g}^{-1}$. Charged electrodes showed values from 1 $\text{m}^2 \text{g}^{-1}$ to 2 $\text{m}^2 \text{g}^{-1}$.

Permeabilities, were determined in an arrangement as shown in Fig. 1. The height of electrolyte h was measured at different time-points 1 and 2 for each electrode. The permeability was then calculated from

$$\mathcal{H}_p = \frac{\mu l}{\rho g(t_2 - t_1)} \ln \frac{h_1 - l}{h_2 - l}$$

which can be derived from Darcys law [10], taking into consideration that the whole pressure drop from the flow is within the electrode thickness l .

3. The electrode system

The solid phase is an interconnected cadmium matrix with a very high electrical conductivity

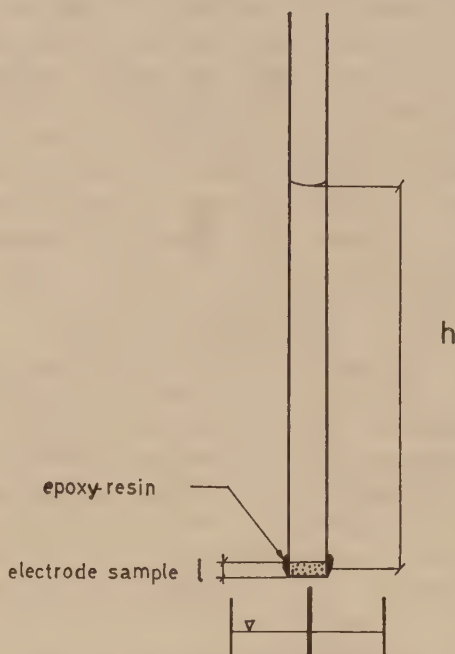


Fig. 1. The electrode permeability column.

solid phase consists of amorphous ferric oxide, which is used as a support. 80% of the metallic particles are in the size interval 0.1–1 μm ; this was estimated with an electron microscope.

The electrolyte phase is considered as an interconnected electrolyte space in the fully charged state. The electrolyte space gradually decreases during discharge according to the positive net change in solid volume which occurs according to the Equation 1.



Basic assumptions made for a high-rate model for porous Cd-electrodes are as follows:

(1) The cadmium matrix is regarded as an iso-potential surface because of the high conductivity relative to the pore-electrolyte conductivity.

(2) The electrode system is regarded as a pseudo-homogeneous two-phase medium. The transport pathways for the species involved in the dissolution-precipitation reactions are regarded as small, compared to the reaction zone within the pore mouth region where the highest reaction current rate initially appears.

(3) The electrode system is regarded as a

in the full charged state. A minor part of the one-dimensional system according to the assumptions just made, and to the electrode design used in the experiments.

(4) Changes in ratio between liquid and solid volume due to precipitation of $\text{Cd}(\text{OH})_2$ are described as quasi-compressible changes in the fixed co-ordinates of the pseudo-homogeneous electrode medium.

(5) The reaction product $\text{Cu}(\text{OH})_2$ is assumed to be rapidly and completely precipitated.

(6) The transport equations for current and mass transports in the electrolyte phase are described by equations from the concentrated solution theory [5].

(7) The electrode is assumed to be isothermal which is confirmed by a check measurement at the current density of 0.2 A cm^{-2} . The temperature increased only 0.2°C during 4 min discharge under thermostatic experimental conditions. The approximation for isothermal conditions is thus within the total experimental error.

(8) The electrolyte gradient outside the electrode is eliminated by means of mechanical agitation.

(9) The time constant for charging the electrical double layer including the reaction transients is small and is of the maximum order of 100 ms for alkaline Cd electrodes. For most discharge transients of technical interest the effects mentioned can be neglected as controlling mechanisms in porous electrodes.

(10) The convection of electrolyte in the electrodes is due to the changing porosity.

(11) The changes in water concentration are relatively small and concentration profiles can be interpolated from electrolyte concentration density relationships.

4. Model equations

During deep discharges or for any thick electrodes it is necessary to include the ohmic polarization in the solid phase. In both these cases the ohmic polarization can be obtained from Equation 2

$$i_1 = -\kappa_1 \frac{d\eta_1}{dx} \quad (2)$$

The ohmic drop within the solid phase is neglected in this work according to the concept of an iso-potential matrix surface.

Thus, in this work η_1 is considered as zero inside the electrode.

The change in concentration of the binary electrolyte, $\text{KOH}(\text{aq})$, is obtained by integration of the one-dimensional simplified version of the general equation for the conservation of the electrolyte (Equation 3).

$$\frac{\partial c}{\partial t} + \nabla \cdot (cv) = \nabla \cdot \left[D \left(1 - \frac{d \ln c_w}{d \ln c} \right) \nabla c \right] - \frac{i \cdot \nabla t_+^0}{z_+ v_+ F} + \frac{v_r}{nF} \nabla \cdot i \quad (3)$$

The derivation of Equation 3 in this form is clearly presented and defined by Newman [5] and is extended here with a source term. Transport mechanisms included in Equation 3 are convection, diffusion and ionic migration. Convection and migration are often neglected beside the source and diffusion terms in low rate models. Migration is a minor term in the chosen transport representation, as t_+^0 has a very low concentration dependence $\nabla t_+^0 \approx 0$ [6] and it is therefore neglected in this high rate-model.

The convection term for the one-dimensional representation is of the form

$$\nabla \cdot (cv) = v \frac{dc}{dx} + c \frac{dv}{dx} \quad (4)$$

when the compressible property of the electrolyte space $\nabla \cdot v \neq 0$ is taken into consideration.

The velocity v is calculated from the continuity equation for electrolyte flow (Equation 5)

$$\frac{\partial v}{\partial x} = -\frac{\partial \varepsilon}{\partial t} \quad (5)$$

Equation 5 is thus consistent with the assumptions made above, regarding the flow in the pore electrolyte. The local changes in porosity are obtained from

$$\frac{d\varepsilon}{dt} = \frac{1}{nF} \Delta \bar{V} \frac{di_2}{dx} \quad (6)$$

Combination of the Equations 5 and 6 gives the differential equation for v ,

$$\frac{dv}{dx} = -\frac{\Delta\bar{V}}{nF} \frac{di_2}{dx} \quad (7)$$

which is to be integrated simultaneously with the transport Equation 8.

The simplified version of the Equation 3 for the one-dimensional case and with the effective coefficient of diffusion, $D_{\text{eff}} = D\varepsilon^{3/2}$ [11], introduced is

$$\frac{\partial c}{\partial t} = D_{\text{eff}} \left(1 - \frac{d \ln c_w}{d \ln c} \right) \frac{d^2 c}{dx^2} - v \frac{dc}{dx} - c \frac{dv}{dx} + \frac{v_r}{nF} \frac{di_2}{dx} \quad (8)$$

The source term in Equation 8 is assumed to be of the form given in Equation 9.

$$\frac{v_r}{nF} \frac{di_2}{dx} = \frac{v_r}{nF} i_0 S g(x)(1-\varepsilon)(1-u) \left[\left(\frac{c}{c_0} \right) \exp(\alpha_a \eta_i) - \exp(-\alpha_c \eta_i) \right] \quad (9)$$

A black-box experimentation with this porous electrode model in conjunction with a study of the steady state kinetics on plane Cd-surfaces has given the result shown. The kinetics on Cd-surfaces are still a challenging area for scientific exploration and the situation has recently been reviewed by Dunning *et al.* [2].

The exchange current density i_0 is related here to the bulk concentration c_0 of the electrolyte and S is the surface activity in cm^2 per cm^3 . A density function $g(x)$ associated with S is introduced to describe the metallic Cd-distribution. The factor $(1-u)$ gives the fraction of the electrode surface which contributes to the current. The variable u is assumed to describe the fraction of pores which will become inactive when the smallest pores cease to function because of their inefficient mass transport ability. For growing local rates, $\partial i / \partial x$, u is growing according to Equation 10.

$$u = k_{bl} \frac{\partial i}{\partial x} \cdot \frac{1}{\varepsilon^{0.5}} \quad (10)$$

The factor $1/\varepsilon^{0.5}$ is assumed to account for a varying quality in the distribution of inter-connected pores for electrodes with different initial porosities. The effect of u is shown later.

The exponent 0.5 is an empirical determination.

The electrode porosity, ε , is treated as a location- and time-dependent state variable. The stoichiometry determines the shift in ε , when applying Faraday's law to differences in mole volumes among solid reactants and reaction products.

The porosity is calculated locally as

$$\varepsilon = 1 - \frac{(1-\varepsilon_0)[(1-y)\bar{V}_1 + y\bar{V}_3 + f\bar{V}_4]}{(1-y_0)\bar{V}_1 + y_0\bar{V}_3 + f\bar{V}_4} \quad (11)$$

ε_0 is the initial porosity distribution. The extent of reaction y , is related to the theoretical capacity Q in the differential Equation 12. y_0 is the initial reaction extent. The solid components in Equation 11 are 1 Cd, 3 Cd(OH)₂, 4 Fe₂O₃.

$$\frac{dy}{dx} = \frac{\int_0^x \frac{di}{dx}}{Q} \quad (12)$$

The changes in surface activity are described as local changes in the g -function (Equation 13)

$$g(x) = g_0(x) - (y(x))^p \quad (13)$$

The exponent p has been recently interpreted by Dunning *et al.* [2] to be a structure-dependent parameter.

$\bar{V}_i$ is the mole volume of each solid component. The factor f expresses the moles of the extender Fe₂O₃ on a cadmium basis.

The ohmic polarization within the electrolyte is obtained and described according to Equation 14, which is an approximation with regard to the concentrated solution theory [5]

$$i_2 = -\kappa_2 \frac{d\eta_2}{dx} \quad (14)$$

The current density i_2 in the pore electrolyte phase is obtained from

$$\varepsilon \cdot \frac{di_2}{dx} = i_0 S g(x)(1-\varepsilon)(1-u) \left[\left(\frac{c}{c_0} \right) \exp(\alpha_a \eta_i) - \exp(-\alpha_c \eta_i) \right] \quad (15)$$

Concentration potentials are obtained from the Nernst equation (Equation 16)

$$\eta_d = \frac{RT}{nF} \ln \frac{a_1}{a_2} \quad (16)$$

In Equation 16 a_1 , the electrolyte activity, is at a reference position outside the electrode and a_2 is the activity at any solution location inside the electrode. Accurate data for KOH (aq) is available in the literature [7].

The various overpotentials are treated analogously to a recently published work by R. Alkire [8]. The total and measured overpotential after compensation for the equilibrium potential is η and is composed as shown in Equation 17.

$$\eta = \eta_1 + \eta_2 + \eta_d + \eta_t \quad (17)$$

where η_1 and η_2 are obtained from integral solutions to Equations 2 and 14 respectively. The charge transfer overpotential, η_t , profile is obtained from Equation 18 as differences based on iterative searches made on the total overpotential η and calculated η_1 , η_2 and η_d profiles

$$\eta_t(x) = \eta - (\eta_1(x) + \eta_2(x) + \eta_d(x)) \quad (18)$$

5. Boundary conditions

At $x=0$, $i_2 = I/\varepsilon$, $c = c_0$ the pore mouth conditions
At $x=1$, the collector conditions are,

$$i_1 = I/(1-\varepsilon), i_2 = 0, \frac{dc}{dx} = 0, \frac{dv}{dx} = 0 \quad (20)$$

The initial conditions for the state variables c , g , ε and y correspond to the initial-time distributions. For a gradient free electrode-electrolyte

$$c(x,0) = c_0 \quad 0 \leq x \leq 1 \quad (21)$$

is valid. The surface density function g varies from electrode to electrode and has the form

$$g(x,0) = g_0 \quad 0 \leq x \leq 1 \quad (22)$$

The porosity distribution is assumed to be uniform,

$$\varepsilon(x,0) = \varepsilon_0 \quad 0 \leq x \leq 1 \quad (23)$$

The reaction extent y is initially zero along the electrode

$$y(x,0) = y_0 = 0 \quad 0 \leq x \leq 1 \quad (24)$$

6. Results and discussion

Typical overpotential transients and their simulations for an electrode with $\varepsilon_0 = 0.414$ in 4.45 M electrolyte are shown in Fig. 2. The best agreement between simulated and experimental transients was obtained for porosities over 0.40.

The charge distribution is shown in Fig. 3, where two examples from the analysed initial profiles are shown. In the estimations $i_0 S(1-\varepsilon)$, experimental charge distributions similar to those in Fig. 3 were applied in a curve-smoothed form. The curve-smoothed relation corresponds to the initial distribution g_0 in Equation 9.

Fig. 4 shows the computer estimated values of the parameter group $i_0 S(1-\varepsilon)$ as a function of the initial porosity. The estimates are based on short-time data, which means 1–2 s after switching on the constant current. The best

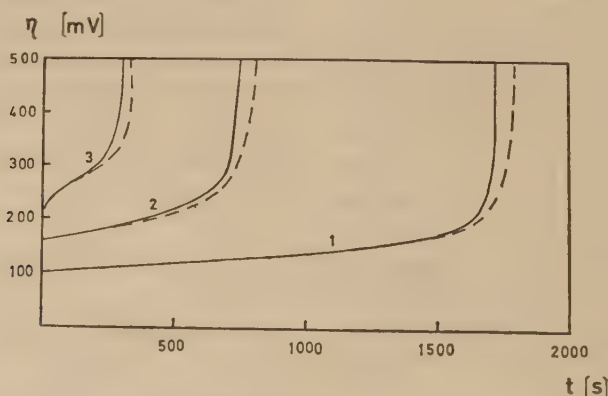


Fig. 2. Simulated and experimental curves for a typical electrode with an initial porosity $\varepsilon_0 = 0.47$ and the thickness $l = 0.152$ cm. The current density is 100, 150 and 200 mA cm⁻² for curves 1, 2 and 3 respectively. Dotted curves are computer simulated transients.

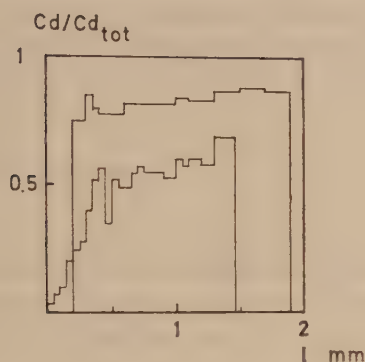


Fig. 3. Two typical initial charge distributions from the electrode sectioned analysis. The backwall co-ordinate is at electrode thickness l . The almost homogeneously charged electrode has the porosity $\varepsilon = 0.72$ and the second electrode is a typical low porosity electrode with $\varepsilon = 0.42$.

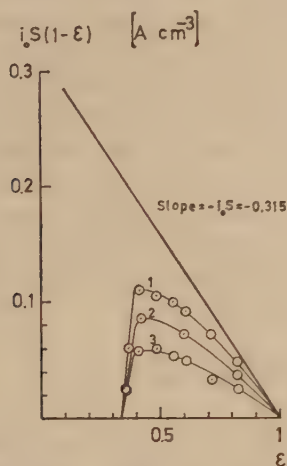


Fig. 4. The electrode activity $i_0S(1-\varepsilon)$ as a function of the porosity in the fully charged state. Curves 1, 2 and 3 represent the experimental values for the constant discharge current densities 100, 150 and 200 mA cm^{-2} . The straight line corresponds to the zero current limit, where $u \rightarrow 0$ when $i \rightarrow 0$, in the expression $i_0S(1-\varepsilon)(1-u)$.

reproducibility was obtained for high porosity electrodes, which also were the more homogeneously charged electrodes.

The straight line drawn in Fig. 4 has the slope $-i_0S$. For the electrodes examined in this work i_0S was determined as 0.315 A cm^{-3} . The curves show the current density influence on the estimated available surface activity $i_0S(1-\varepsilon)$ before the introduction of the load dependent variable u . It may be of importance to

point out that i_0S can be dependent on the preparation, and on the precision of the selected g -profiles. The amount of extender and possible binding materials, which are the usual components in commercial electrodes, can also be of importance. The electrodes in this work are all of the same composition and prepared with the uniform procedure described above. The constant $k_{b1} = 0.42$ was found from a least square analysis applied to Equation 10.

Low porosity electrodes gave large deviations from the relation $i_0S(1-\varepsilon) \cdot (1-u)$. The deviation from the last relation at porosities lower than 0.39 is interpreted as an effect of ineffectively interconnected electrolyte space which occurs in a region where the particles are closely packed. The specific current load in the residual pores thus increases the polarization at the expense of the ineffectively connected pores.

In general it is difficult to predict where the critical porosity limit appears and it can be expected to be dependent on the composition and structure of the active material. The observed limit is 0.35 which is for the electrode mixture examined in this work.

Fig. 5 shows high rate overpotentials at different time points as a function of the initial porosity for electrodes of comparable thickness.

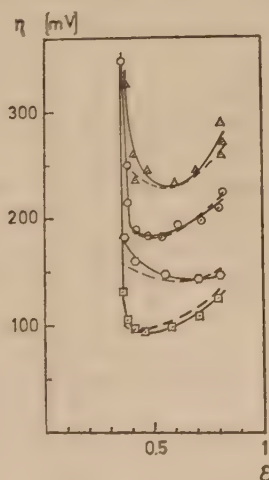


Fig. 5. Overpotentials at different time points for electrodes prepared with different porosities in the charged state. The electrode thickness is $l = 0.160 \pm 0.010 \text{ cm}$. Dotted curves are computer simulations. Experimental values are $\square$ 20 s, 100 mA cm^{-2} ; $\circ$ 1200 s, 100 mA cm^{-2} ; $\circ$ 20 s, 200 mA cm^{-2} and $\triangle$ 180 s, 200 mA cm^{-2} .

During short periods of time, polarization increases with increasing initial porosity. The explanation is that the electrode activity $i_0 S(1-\varepsilon)(1-u)$ decreases with increasing ε . The latter gives rise to an increasing internal surface load resulting in increasing polarization. At long discharges the electrodes will be exhausted, because of the insufficient transport of electrolyte from the bulk into the electrode inside.

Essentially two conditions define the exhausted state, reactant depletion from pure mass transfer limitations and precipitation of an insoluble reaction product $\text{Cd}(\text{OH})_2$ causing restricted mass transfer.

For high rate cases, $i=200 \text{ mA cm}^{-2}$, the concentration depletion is the controlling mode. This causes increasing ohmic and concentration polarizations together with a lowered reaction velocity. Low porosity electrodes are more sensitive to different load conditions than medium porosity electrodes because of the weaker transport abilities for both current and mass in the electrolyte phase. The larger reaction surface for low porosity electrodes does not compensate for the ineffective transport properties. The model predicts the general minimum polarization curve shape for varying porosity.

Precipitation of the insoluble $\text{Cd}(\text{OH})_2$ as a primary cause of polarization increase is obtained at lower discharge loads. Experiments performed at 100 mA cm^{-2} gave the latter polarization effects. The mechanism can be described as a continuous plugging of the pores in the pore mouth zone followed by an electrolyte depletion caused by the hindered mass transport. This phenomena has recently been treated independently by Dunning [2] and Simonsson [3] and in this work their explanations are confirmed.

In order to test the arguments for the different exhausting mechanisms described above which were predicted in the model for various load levels, some electrolyte permeability experiments were performed. Table 1 gives a comparison between two electrodes with almost identical physical properties. The electrodes were discharged to 500 mV final polarization. The permeabilities were measured according to the procedure described above.

Table 1 shows that the permeability at the

Table 1. Electrolyte permeabilities

$I(\text{mA cm}^{-2})$	$\kappa_p \cdot 10^{10} \text{ cm}^2$	ε_0	$\varepsilon_{\text{pore mouth}}$
100	0.32	0.53	0.36
200	1.15	0.51	0.45

final states is different for the two load levels. The κ_p value for the 100 mA cm^{-2} case together with the simulated final value of $\varepsilon_{\text{pore mouth}}$ indicates that this electrode is influenced by the precipitation of $\text{Cd}(\text{OH})_2$ which is not the case for the other electrode at 200 mA cm^{-2} . The interval of $100\text{--}200 \text{ mA cm}^{-2}$ seems to be a transition interval from pore blockage to pure mass-transfer limitations.

The exponent p in Equation 13 is of general importance in the simulation of the experimental curves. In this work p has been found to fit the data best when $p = 0.80 \pm 0.05$. The sensitivity of p increases with increasing current density. At $i = 100 \text{ mA cm}^{-2}$ there was no significant difference between $p=1$ and $p = 0.80$ within the experimental error. At $i = 200 \text{ mA cm}^{-2}$, ($p=0.80$), p became a sensitive parameter. $p=1$ almost doubled the discharge time compared to $p=0.80$ at $i=200 \text{ mA cm}^{-2}$.

7. Solutions of equations

The solutions to the coupled Equations 7, 8 and 10–15 were obtained from an implicit finite-difference representation of the equations. These were iterated for the imposed constant current condition and for the given boundary conditions (Equations 19 to 24). A useful numerical method has been devised by Newman [9] which is suitable for treating complex coupled equations.

8. Conclusions

The model presented is based on rough simplifications concerning the microkinetical situation which is to be included in a more exact model. Another important extension to the model for general applications is to introduce the effects of pore size distributions which in this work are introduced empirically. The model gives a good

explanation of the influence of porosity on mass transfer and on surface activity for high-rate discharges, for the electrode mixture examined in this work.

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Analysis of porous alkaline Cd-electrodes.

II. Potential recovery transients after a period of discharge

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The recovery of the diffusion potential after a period of discharge is analysed for porous Cd-electrodes. A composite process with discharge-idle time and discharge is simulated and compared with an experimental process. The general influence of porosity on charge capacity is examined in a charge porosity diagram.

Nomenclature

o initial time
w water as solvent

Symbols

a electrolyte activity
c concentration of the binary electrolyte KOH
mol cm⁻³
D diffusion coefficient, cm² s⁻¹
F the Faraday constant, 96487 As per mol
equiv.
l electrode thickness, cm
R universal gas constant, 8·3143 J K⁻¹ mol⁻¹
t time, s
T temperature, K
x position co-ordinate, inside the electrode,
cm

Greek

γ activity coefficient
 η overpotential

Subscripts

b bulk electrolyte
d diffusion
eff effective

1. Introduction

Until now there has been no analysis of porous electrodes in the current free state after an active current period. The recovery of the electrodes after an active current state is of great importance in various engine-cranking applications. Therefore it is of interest to analyse the currentless state in order to be able to simulate a chain of cranking and idle-time periods. A specification of general cranking conditions for various engines is presented by U. Falk and A. Salkind [1]. In this work some results are shown for the porous electrodes which are described earlier in an analysis of transients in the active state. [2]

In this work the diffusion of reactants from the bulk electrolyte into the electrodes is the considered potential recovery mechanism. The electrodes are also considered to be free from porosity changes during the recovery time. Diffusion is supposed to be of importance at intervals of a half second to about an hour. The technical cranking procedures are mostly within the specified interval of time. Here the potential transients are conclusively interpreted as pure concentration potential transients.

2. The model

The basic model is the same as described in an earlier paper [2]. As there is no species source in a currentless state the mass conservation equation for a one-dimensional electrode, with a binary electrolyte, will be as follows:

$$\frac{\partial c}{\partial t} = D_{\text{eff}} \left(1 - \frac{d \ln c_w}{d \ln c} \right) \frac{d^2 c}{dx^2} \quad (1)$$

The concentration transients inside the electrodes are obtained from the solution of Equation 1 for the following boundary conditions, at the time t_0 ,

$$c(x, t_0) = c_0(x) \quad 0 \leq x \leq 1 \quad (2)$$

which is the concentration profile inside the electrode at the current breaking moment t_0 .

At the collector $x = 1$ the insulation condition (Equation 3) is valid,

$$\frac{dc(l, t)}{dx} = 0 \quad t \geq t_0 \quad (3)$$

The bulkside condition $x = 0$ is for a well-stirred bulk electrolyte,

$$c(0, t) = c_b \quad t \geq t_0 \quad (4)$$

Analytical solutions to this problem are in general not easy to obtain, because of the general and non-linear form of the initial distribution condition (Equation 2).

The diffusion potential transient is obtained from the numerically solved concentration profiles calculated with the Nernst equation (Equation 5)

$$\eta_d = \frac{RT}{nF} \ln \frac{a_1}{a_2} \quad (5)$$

where a_1 is the electrolyte activity at the reference electrode position and a_2 is the minimum activity inside the electrode. The latter activity is calculated from the concentration profile according to Equation 6. The minimum concentration is not in general equivalent to the minimum activity [5].

$$a = \gamma c \quad (6)$$

The solution to Equation 1 with the given boundary conditions is solved by the numerical method mentioned earlier [2].

3. Results and discussion

Fig. 1 shows experimental and simulated potential recovery transients for some electrodes.

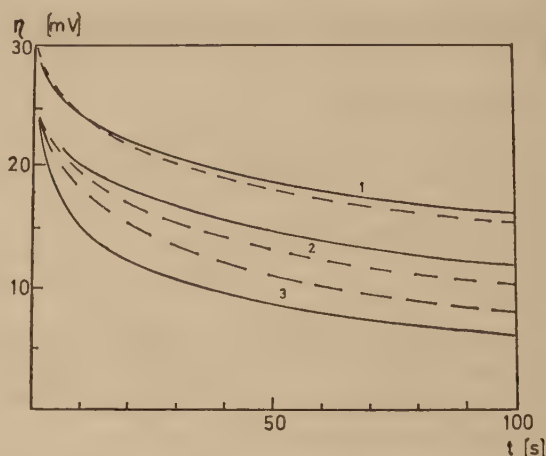


Fig. 1. Experimental and simulated diffusion potential recovery transients after deep discharges for three different porous Cd-electrodes. Curve 1 is an electrode with the thickness $l = 0.080$ cm and the porosity $\epsilon = 0.35$, curve 2 an electrode with $l = 0.1$ cm and $\epsilon = 0.65$. Curve 3 and electrode with $l = 0.15$ cm and $\epsilon = 0.75$. The given porosities are mean porosities at final discharge. $D_{\text{eff}} = \epsilon^{3/2} D$ is applied. Simulated curves are shown as dotted lines.

The differences in recovery between the electrodes shown are explained by differences in mass transport properties. The curves 1 to 3 show the influence of porosity on the recovery dynamics. As one would expect, the high porosity electrodes have the best recovery ability. The coefficient used for the calculation of the effective diffusion coefficient, D_{eff} , was $\epsilon^{3/2}$ [6]. The initial porosity and concentration profiles were calculated with the dynamical model [2] described earlier.

Fig. 2 shows an experimental and simulated chain of discharge-recovery and discharge, in order to demonstrate the potential possibility to describe complex transient processes with the model simulation technique. The simulation of the processes just described for porosities greater than 0.45, was successful. Deviations appeared for the lower porosities in the simulation of the second discharge period. The model predicted, in general, lower polarizations than were measured. The unsuccessful simulation of a low

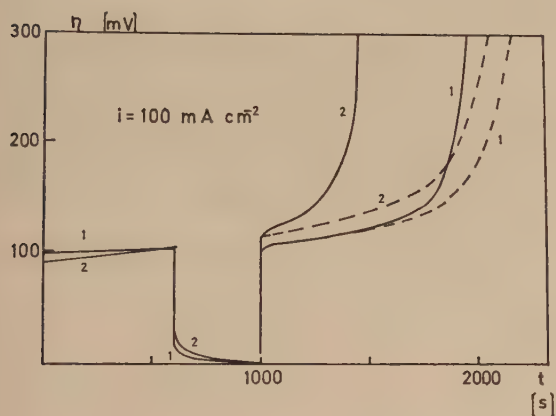


Fig. 2. Comparison of experimental and simulated combined processes composed of a 600 s long discharge, 400 s recovery and a final discharge. Dotted curves are simulations. Curve 1 is an electrode with $\epsilon = 0.53$, $l = 0.190$ cm. Curve 2 is a low porosity electrode with $\epsilon = 0.41$ and $l = 0.180$ cm.

porosity electrode is shown in the diagram. A possible explanation for the failure can be that the basic model does not accurately describe the controlling processes, in the region where the pores are no longer properly connected.

A possible interpretation of the unsuccessful simulation could be that the active surface was blocked by precipitated $\text{Cd}(\text{OH})_2$ from a supersaturated cadmate electrolyte during the idle time. The effect of marginal precipitation can be expected to be greatest for low porosity electrodes because of the disconnected pores. This has been discussed previously [2].

A study of the situation in a charge–porosity diagram can give a broader view. The charge–porosity diagram has been described earlier in this journal [3].

The critical porosity is defined as the porosity where an electrode almost loses reaction activity in the fully charged state. The region where the porosity becomes critical is in the region where the electrolyte phase begins to be disconnected by close packing of the solid phase. The characteristic critical porosity for this electrode material and preparations is found to be close to 0.34. This limiting value is shown as the vertical line 2 in Fig. 3, which shows a low porosity electrode on the discharge line 1. The low porosity electrode follows line 1 at discharge from the initial point *a* to the final point *b* in a pure discharge

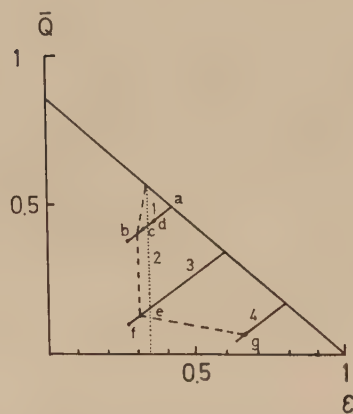


Fig. 3. A charge – porosity diagram for $\text{Cd}/\text{Cd}(\text{OH})_2$ with Fe_2O_3 as the inert material. The full charge line is drawn for 90 w % CdO and 10% Fe_2O_3 . The characteristic discharge slope $d\bar{Q}/d\epsilon$ is 0.745. The dotted line corresponds to final states at 75 mA cm^{-2} from fully charged states.

process at 75 mA cm^{-2} . Point *c* is obtained as the final point in a composite process with discharge to *d*, one hour idle at *d* and a final discharge to *c* where the electrode is polarized infinitely.

Line 3 shows an electrode with the initial porosity of 0.60, which is the usual level in commercial electrodes; the corresponding final state is predicted to point *e*. The discharge efficiency for the last process is calculated from the diagram to be about 60%. In practice such electrodes will have around 70% utilization [4]. The latter efficiency is shown as point *f*.

High porosity electrodes, as pointed out earlier do not show the previously discussed effects which can also be expected from the charge–porosity diagram. Line 4 for an electrode with a porosity of 0.75 which nowhere reaches the limiting value $\epsilon = 0.34$ within the obtained efficiency 0.60. The latter corresponds to point *g*. The dotted boundary line *h* shows the final states for the examined electrodes at the constant current level of 75 mA cm^{-2} .

4. Conclusions

The recovery of the potential can be predicted by means of numerical mass transfer models for known initial concentration and porosity profiles inside porous electrodes. It should be

possible to analyse commercial electrode materials in the same way as in this analysis in combination with the previous analysis. The analysis could also be implemented on other similar electrode systems such as alkaline zinc and iron electrodes and on the lead-acid system. The charge-porosity diagram can be regarded as an efficient means of storing comprehensive information on electrode systems.

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Analysis of porous alkaline Cd-electrodes.

III. The application of charge porosity diagrams in electrode design

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A simple charge-porosity diagram is presented for the rapid estimation of charge capacity in battery electrodes. Porosity changes reflect differences in mole volumes of the reactants and reaction products. Each system has a specific sensitivity to porosity changes. This diagram can be a useful tool for the assessment of mass and current transport performance of electrodes that give insoluble reaction products. Alkaline Cd, Zn and Fe electrolytes are compared.

Nomenclature

Symbols

c	electrolyte concentration mol cm ⁻³
F	the Faraday equivalent, As per mol equiv.
I	current, A
M	mole weight
$\bar{Q}$	normalized charge density, dimensionless
R	reactant balance ratio between matrix and electrolyte phases
t	time, s
V	electrode volume, cm ³
$\bar{V}$	partial mole-volumes, cm ³ mol ⁻¹
(s)	solid phase
(aq)	aqueous phase

Greek

ε	porosity
ρ	density, g cm ⁻³
ν	stoichiometric coefficients

Subscript

i	species i
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1. Introduction

For the optimization of electrode composition

it is important to establish the effects of the various components on the total result. The present paper gives a simple analysis based on stoichiometry, on Faraday's law and on differences in mole volumes of the different materials used in order to show some fundamental relations between capacity and porosity.

Many electrode systems have a simple basic structure with a solid consumable matrix phase and a liquid electrolyte phase that also functions as the conducting element and as the reactant supply. In most systems the solid phase reactants are present in great excess over the electrolyte phase reactants. Normal electrode systems thus have to rely on mass transport of reactants to maintain stoichiometry. This can be illustrated with the alkaline Cd/Cd(OH)₂ system (Equation 1). The theoretical equivalents in the solid phase can be compared with the liquid phase equivalents using the ratio R found from Equation 2.



$$R = \frac{2\rho_{\text{Cd}}(1-\varepsilon)}{M_{\text{Cd}}C_{\text{OH}^-}\varepsilon} \quad (2)$$

When $R=1$ the stoichiometry is balanced in the initial state. Equation 3 gives the porosity

corresponding to the stoichiometric balance exemplified for 5 M alkaline electrolyte.

$$\varepsilon_{R=1} = \frac{1}{1 + \frac{c M_{\text{Cd}}}{2 \rho_{\text{Cd}}}} = \frac{1}{1 + \frac{5 \cdot 10^{-3} \times 112.4}{2.8 \times 64}} = 0.97 \quad (3)$$

The high porosity value obtained for the Cd/Cd(OH)₂ case shows the importance of mass transport for the complete consumption of electrodes of considerably lower porosities. Equation 4 relates the normalized charge capacity $\bar{Q}$ to the electrode porosity in the fully charged state.

$$\bar{Q} = 1 - \varepsilon \quad (4)$$

2. Variations in porosity

Consider a discharge process where the solid volume of the reaction products is greater than that of the reactants. Different situations can occur depending on the initial conditions and on the magnitude of the absolute volumetric changes. In the case of a constant stoichiometric change $\Delta \bar{Q}$, there are three possibilities to be considered:

- (i) a decrease in porosity
- (ii) a decrease to zero porosity
- (iii) a decrease to zero porosity accompanied by an increase in volume

The final state in case (i) must correspond to a higher initial porosity than that in cases (ii) and (iii). The least favourable case (ii) occurs with a fixed electrode volume with all the precipitated discharge product occupying the initial volumes of electrolyte and reacted solid matrix. Any subsequent increase in volume (case iii) is of lesser concern here and only cases (i) and (ii) need be considered.

3. The charge-state diagram

The porosity-changes can be visualized in a simple porosity-charge diagram, relating normalized charge capacity to porosity. Line 1 in Fig. 1 indicates the fully-charged state corresponding to a completely charged matrix phase. Equation 4 is the basic equation for this tie-line. The point *a* indicates the initial state, ε_i . A change in

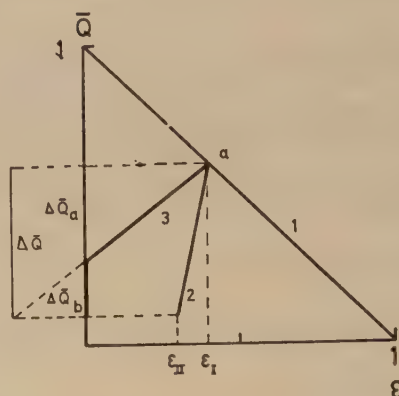


Fig. 1. Different discharge lines for a constant porosity charge change $\bar{Q}$.

charge, $\Delta \bar{Q}$, will follow the line 2, the discharge working line, to give the final state ε_{ii} . This final state will be characterized by the residual charge and a porosity $\varepsilon > 0$. This is case (i) with unblocked final state. In case (ii), the discharge working line, drawn from the same base point, will intersect the $\bar{Q}$ -axis before reaching the theoretical total change in $\bar{Q}$. The crossing point gives the capacity at the point where the porosity disappears. Any continued change in $\bar{Q}$ beyond the crossing point will follow the zero-porosity line and will be accompanied by volume expansion (i.e. case iii). It can be shown that the distance along $\bar{Q}$, at $\varepsilon = 0$, will be proportional to the volume change and is given by

$$V_{ii} = \frac{\Delta \bar{Q}_a + \Delta \bar{Q}_b}{\Delta \bar{Q}_a} V_i \quad (5)$$

where the coefficient of V_i is the volume factor.

The derivative $d\bar{Q}/d\varepsilon$ is a constant for a given system when the mole volume change is linear. The three cases analysed here thus belong to different systems. Fig. 2 shows three cases for the same system when different initial porosities are taken. The lines 4 to 6 will show parallel shifts with increasing initial porosity.

Case 4 is for a high capacity system with a porosity restriction allowing only low charge withdrawal. An electrode design of this type may be appropriate for low power intensity applications. The blockage of the matrix phase, which will occur at high utilization, will not allow high mass transport from the bulk electrolyte into the electrode. Case 5 is a boundary

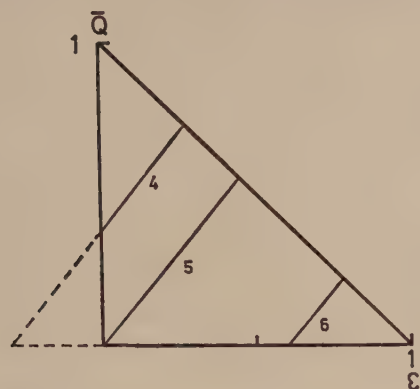


Fig. 2. Discharge lines for different initial porosities in a given system.

situation for maximum charge delivery without blockage. Here the designer will start from the origin of the diagram and draw a discharge line with the slope $d\bar{Q}/d\epsilon$ characteristic of the system, to the full charge line. The corresponding porosity will be the lowest acceptable initial porosity. For high rate applications, case 6 applies where a high final porosity level is required in order to retain good mass transfer rates. Good transport characteristics imply inevitably that the built-in capacity will be low.

4. The effect of inert materials

Obviously, the built-in capacity will be affected by the addition of inert, passive materials. Among these will be extenders, binders and non-reacting solids added to improve conductivity.

The full charge line for a system that includes inert materials is easy to construct if the electrode composition is given on a volume fraction basis. A line from the right corner ($\epsilon = 1$, $\bar{Q} = 0$) is drawn to a point on the $\bar{Q}$ -axis corresponding to the volume fraction of the active materials at zero porosity (Fig. 3). The full charge line shown in Fig. 3 for the cadmium system is for a 10% inert material content. As shown in the following section the gradient of the discharge line is not affected by the proportion of passive material.

5. The discharge line

A simple derivation of the equation for the dis-

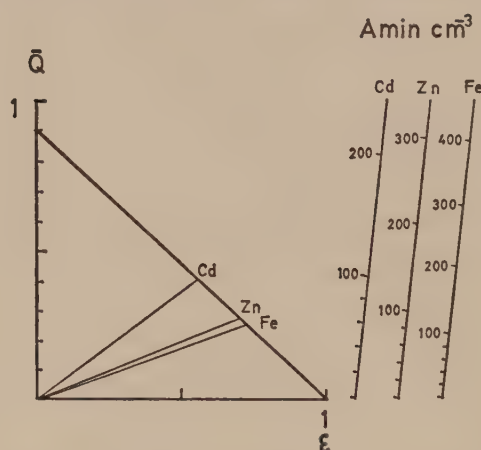


Fig. 3. Charge-porosity diagram with 10% passive material. Characteristic discharge lines are shown for $\text{Cd}|\text{Cd}(\text{OH})_2$, $\text{Zn}|\text{Zn}(\text{OH})_2$ and $\text{Fe}|\text{Fe}(\text{OH})_2$ to give lowest acceptable initial porosities for high rate applications.

charge line is given here to demonstrate the properties of this line. Consider a reaction such as 1 giving a unit charge transfer of 2 F. Contributions to the volume change in the solid phase will come only from the species Cd and $\text{Cd}(\text{OH})_2$. The volume change for a current I and a duration of Δt time units can be expressed in terms of mole volumes, $\bar{V}_i$, so that the volume change for the solid-phase, $\Delta V(s)$, will be

$$\Delta V(s) = (\bar{V}_{\text{Cd}(\text{OH})_2} - \bar{V}_{\text{Cd}}) \frac{I\Delta t}{2F} \quad (6)$$

When related to the system volume V , this gives the porosity change, $\Delta \epsilon$

$$\Delta \epsilon = \frac{\Delta V(s)}{V} \quad (7)$$

The corresponding relative change in capacity for a quantity of charge, $I\Delta t$ will be

$$\Delta \bar{Q} = \bar{V}_{\text{Cd}} \frac{I\Delta t}{2F} V^{-1} \quad (8)$$

The derivative $d\bar{Q}/d\epsilon$ (Equation 9) can be obtained from Equations 6–8 after simplification

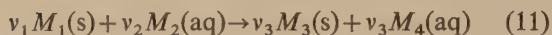
$$\frac{d\bar{Q}}{d\epsilon} = \frac{\bar{V}_{\text{Cd}}}{\bar{V}_{\text{Cd}(\text{OH})_2} - \bar{V}_{\text{Cd}}} \quad (9)$$

The discharge line for the $\text{Cd}|\text{Cd}(\text{OH})_2$ system shown in Fig. 3, will have a gradient 0.745, when mole volumes are calculated from

densities and molecular weights according to the equation.

$$\bar{V}_i = \frac{M_i}{\rho_i} \quad (10)$$

For the general reaction (Equation 11) the discharge line can be calculated from Equation 12.



$$\frac{d\bar{Q}}{d\varepsilon} = -\frac{\bar{V}_1}{v_3 \bar{V}_3 + v_1 \bar{V}_1} \quad (12)$$

No change in porosity will occur when there is no net change in volume. The denominator then has value zero. This will happen when

$$v_3 \bar{V}_3 = -v_1 \bar{V}_1 \quad (13)$$

For a dissolving electrode with soluble reaction products, $v_3=0$, the gradient will be negative, reflecting the increasing porosity. If during discharge some of the current goes into producing soluble species, the $d\bar{Q}/d\varepsilon$ curves will lose the contact with the curves based on insoluble reaction products. Zinc electrodes in concentrated hydroxide solutions can be expected to show deviations caused by the soluble zincate complex-ion $\text{Zn}(\text{OH})_4^{2-}$. Cadmium and iron electrodes are expected to have very small

deviations between the theoretical and actual $d\bar{Q}/d\varepsilon$ curves.

6. Absolute capacity

A nomogram showing the absolute charge capacity can easily be added to a normalized charge-porosity diagram by adding appropriate scales to each electrode system as shown on the right in Fig. 3. This shows absolute scales for $\text{Cd}|\text{Cd}(\text{OH})_2$, $\text{Zn}|\text{Zn}(\text{OH})_2$ and $\text{Fe}|\text{Fe}(\text{OH})_2$.

From Fig. 3 it is apparent that the $\text{Fe}|\text{Fe}(\text{OH})_2$ system is the most sensitive to porosity changes, while the $\text{Cd}|\text{Cd}(\text{OH})_2$ system is the least sensitive to changes in capacity $\bar{Q}$. A comparison on a relative basis is somewhat misleading for practical situations as the absolute charge follows the reverse order for the metals compared here. An absolute change of 50 A min cm^{-3} from a fully charged initial state will give final porosities of 0.30 for Cd and Zn and 0.43 for Fe. It is thus of some importance to compare different systems on an absolute scale in order to assess the porosity effects.

Acknowledgement

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ANALYSIS OF POROUS ALKALINE Cd-ELECTRODES

IV Optimization of current efficiency

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Abstract

Optimization of the electrode-thickness, porosity and the amount of active material necessary for a defined electrode polarisation is carried out with a mathematical model on porous Cd-electrodes. Three different problems were formulated for a constant current-load and a specified final total polarisation in order to maximize the utilization of active materials. The results obtained show that the best high rate electrodes (100 mA/cm^2) are high porosity electrodes with the half-width thickness in the interval of 0.10-0.18 cm depending on the formulated optimization problems.

INTRODUCTION

The materials used in battery electrodes are usually expensive and this gives motivation to search for more efficient electrode designs. Electrodes in high rate applications have generally the poorest utilization of the active material and it is therefore important to analyse their design. Attention is drawn here to the porous high rate Cd-electrodes, which have been presented recently, [1], as an example of a simple optimization analysis.

The distribution of the active material in the geometrical cell body is important in the design of efficient batteries. The problem of distribution can conveniently be divided into two groups of problems; local and global, depending on their influence on the physical cell design. A local design problem can be given by an attempt to find the combination of porosity and electrode thickness, which gives the best utilization of the active material. An example of global electrode design problem is the treatment of the compromise between a small number of large electrodes and a large number of small electrodes for various amounts of active material.

The porous electrode which is to be optimized in this analysis has an open and planar structure. The open structure gives an electrode free from the diffusion and current restrictive geometrical influence which often are associated with commercial electrode constructions in which the active material are enclosed in various ways. The envelopes are usually of the perforated pocket type [2].

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By selection of the undisturbed electrode structure it is possible to obtain results which represent the ultimate limit of criteria for a chosen sample of the active material. The open structure thereby represents the ideal prestanda which can be of value when compared with the technical electrodes.

2. ANALYSIS

From the theoretical and experimental analysis of porous electrodes it is well-known that high current loads give non-uniform and poor utilization of the active materials [3, 4]. Non-uniform current distributions occur predominantly for thick electrodes. Therefore an obvious way to increase the utilization of the active material would be to decrease the electrode-thickness. A decrease in the electrode thickness in general leads to an increased electrode polarisation at constant load conditions. Figure 1 shows the importance of the electrode thickness for the polarisation at a constant current load. Figure 1 shows that it is possible to obtain a low polarisation with a large amount of the active material. It is possible to formulate several problems with almost the same goals and it is necessary to some extent to discuss the problem-analysis and the influence of the various criteria on the electrode design.

For electrodes based on expensive materials it is obvious to compare current-efficiencies. It is convenient to make the comparison of efficiency from various constant current loads and for various final polarisation levels. The polarisation levels are to be chosen with regard to specified technical applications. A polarisation of 200 mV is in this work assumed to be reasonable for high rate discharges, (100 mA/cm^2). The ratio of the capacity

consumed, for a given maximum polarisation, to the total available capacity gives the utilization efficiency (equation 5). Another way is to compare efficiencies at a fixed interval of time. The latter is usually applied in cranking applications.

The given concept of current efficiency gives no information on the way in which an electrode is to be constructed and in order to overcome this lack of information it is necessary to describe the utilization of the electrode volume. For a local optimization problem, which is the main interest here, it is practical to let the system volume be composed of a half-electrode, l , together with a half electrolyte channel, d , including the current collector in the electrode. Figure 2 shows the system volume for one electrode. From this division of the system volume there is only the electrode thickness in combination with the electrode porosity as variables to affect the capacity. The capacity within the system volume is Q A.min. The amount of active material corresponding to Q can be related to two different projections which both express compactibility. When the capacity Q is projected perpendicular to the load-current direction, the measure $Q(a)$ A.min/cm² is defined. The measure $Q(b)$ A.min/cm² is defined from the projection of capacity Q on the base area. In $Q(b)$ consideration is given to the effect of passive construction elements, such as the channel electrolyte and the collector, which is not the case within $Q(a)$. $Q(b)$ belongs more than $Q(a)$ to the global analysis where the electrode height together with the electrode thickness is the central problem. Therefore the attention is drawn here primarily to the measure $Q(a)$ as it is a local problem.

2.2 Relations between design variables and capacity

The equation which gives the capacity of the system volume is

$$Q(a) = q \cdot l \quad (1)$$

where q is the volume capacity of the active material in A.min/cm³. The system volume considered here, is $1 \cdot 10^2$ cm³ (1 cm² electrode area).

The capacity q is dependent on the porosity and the theoretical capacity q_0 according to equation (2)

$$q = q_0(1-\epsilon) \quad (2)$$

With q from (2) introduced in equation (1) $Q(a)$ is explicitly expressed in l and ϵ , which is shown in equation (3)

$$Q(a) = q_0(1-\epsilon)l \quad (3)$$

$Q(b)$ is obtained in an analogous way, equation (4).

$$Q(b) = q_0(1-\epsilon) \frac{1}{1+d} \quad (4)$$

A comparison between (3) and (4) for a constant electrolyte-channel and collector shows that $Q(a)$ and $Q(b)$ are lineary proportional.

2.3 Variable constraints

In all optimization analysis it is necessary to specify the allowed intervals of the design variables. To be considered in the following are the limits for the electrolyte channel d , the charged electrode porosity ϵ , the theoretical capacity q_0 and electrode thickness l .

The width of the electrolyte channel d , has the lower limit determined by the buffer capacity of the electrolyte against concentration changes. This argument can be neglected at short-time discharges. A common channel measure with the collector included is about 1 mm, which corresponds to $d = 0.5$ mm according to the definition used for d . The interval $0.25 \leq d \leq 0.5$ is selected here.

The electrode porosity ϵ has an upper limit dependent on mechanical properties. The upper porosity limit is 0.85 which corresponds to the upper limit in the experimental investigations made on this active material [1]. The lower porosity limit is 0.40 and is selected with respect to the drastic reduction of the accessible active surface which occurs below this value. The interval $0.40 \leq \epsilon \leq 0.85$ corresponds to the design porosities allowed here for charged electrodes.

The theoretical capacity q_0 is given with regard to the amount of active material in the solid phase. In this investigation q_0 has the constant value $218 \text{ A}\cdot\text{min}/\text{cm}^3$ and corresponds to the experimental electrode material mentioned above, which has the volume fractions on solid phase basis as 0.86 Cd and 0.14 Fe_2O_3 .

The interval is not specified for the electrode thickness as it is of primary interest to find thicknesses which give minimum polarisations.

3. FORMULATION OF PROBLEMS

Three problems representative of the local analysis are dealt with here.

Problem I

Determine the capacity $Q(a)$ which gives the best utilization of the active material for given current load and final polarisation conditions.

Problem II

Determine the smallest capacity $Q(a)$ for a given current load and a given limit on final time and final polarisation.

Problem III

Determine the capacity $Q(b)$ which gives the best utilization of the active material for a given current load and final polarisation conditions.

The efficiency values for the different problem basis $Q(a)$ and $Q(b)$ are calculated from the equations (5) and (6) which define the various efficiency measures:

$$\eta_{Q(a)} = \frac{I t}{Q(a)} \quad (5)$$

$$\eta_{Q(b)} = \frac{I t}{Q(b)} \quad (6)$$

I is the constant current load per surface-unit and t is the time elapsed until the polarisation has reached a selected value. In problem II the time is also a prefixed quantity and is called final time. The method of finding solutions to the problems is based on successive variations of the variables l , ϵ , q_0 and d with selection of the best combination and with regard to the variable restrictions.

4. EVALUATION OF OPTIMAL SOLUTIONS

Problem I

The evaluation of the results from variation of the variable calculations can conveniently be handled in a diagram. Figure 3 shows a collection of virtual $\eta_{Q(a)} - Q(a)$ curves with the electrode thickness as a parameter for defined current and polarisation conditions. In the figure there is also a curve drawn representing the tie line for all the maximum points connected with the different electrode thicknesses. The optimal solution to problem I corresponds to the maximum on this later tie-curve. The lower limit on $Q(a)$ is alternatively determined by the maximum allowed design-porosity or by the direct influence from the final polarisation condition. The latter corresponds to $\eta_{Q(a)} = 0$ for $\epsilon < \epsilon_{\max}$ and the former to $\epsilon = \epsilon_{\max}$. The upper limit is solely determined by the present polarisation condition.

Problem II

In order to find optimal solutions to problem II it is convenient to extend the $\eta_{Q(a)} - Q(a)$ diagram with curves according to equation (7)

$$\eta_{Q(a)} = \frac{I t}{Q(a)} = \frac{K}{Q(a)} \quad (7)$$

In equation (7) the constant K is characteristic for the constant current load I and the fixed final time t , for which the minimization of $Q(a)$ is performed.

Hyperbolas according to equation (7) are introduced in figure (5). The intersections between the hyperbolas and the different thickness curves give values on $Q(a)$ which satisfy the final time conditions for different electrode thicknesses. For double intersections one has to take the

smallest $Q(a)$ value to obtain an suboptimal solution. The best solution and the solution to problem II can be obtained from a diagram where the sub-optimal solutions for all electrode thicknesses are collected and from which the smallest $Q(a)$ value is to be chosen.

Problem III

For a constant channel-width d , $Q(a)$ and $Q(b)$ are linearly proportional which gives similar solutions for problem I and III. By variation of d a number of different solutions to problem III can be obtained and from these the best solution is to be selected. This sequence has not been carried out here, as the selection of an electrolyte channel d has also to be considered in conjunction with other effects such as variations in the electrolyte-concentration. Another way to affect $Q(b)$ is to discretise the system volume into a number of equal parts. Each part has an electrolyte channel d , which has the same measure as in the original system volume. This method of division gives reduced space for the active material. Figure 4 shows the effect of the division for one to four sections. The effect of the introduction of electrolyte channels on the utilization of base cell volume can be extracted from the constant value, $l + d = 0.25$ cm. This latter value is proportional to the base cell volume. The draw-back arising from reduced electrode space, is logically balanced by the advantage of giving sections with lowered section current loads for a constant current load to the whole system volume. Equation (8) gives the section current density as a function of the division number N and the nominal current load I .

$$i_N = \frac{I}{N} \quad (8)$$

Sectioning as a method to obtain better electrodes has to be proved against the consequences for the counter-electrode. The latter electrode is ignored in this analysis.

If, the counter-electrode is the limiting electrode, then sectioning is not an applicable method, as the counter electrode will become the limiting part of the system.

If the counter electrode has equal or better polarisation properties, sectioning can be a valuable analytical method for the system. The usual counter-electrode to the alkaline Cd-electrode is the NiO(OH)/Ni(OH)_2 electrode, which fulfils the condition as a better electrode at short discharge time intervals, but is the limiting electrode at deep discharges.

5. RESULTS AND DISCUSSION

The electrode polarisations were calculated with the numerical model described previously [1]. The calculations were made for a temperature of 22°C and the electrolyte concentration was 4.45 M KOH.

Problem K

Figure 5 shows $\eta_{Q(a)} - Q(a)$ curves with the electrode thickness as parameter for 100 mA/cm^2 and 200 mV final-polarisation. The tie-curve for maximum points is given together with hyperbolas for different final time limits. On the basis of figure 5 it is possible to solve problems I and II. For problem I the best efficiency $\eta_{Q(a)}$ is obtained at 11.4 %, which occurs for $Q(a) = 8.8 \text{ A.min/cm}^2$. The corresponding optimal electrode-thickness is difficult to determine from the diagram. A simpler way of determining the thickness, is to plot the maximum efficiencies for all electrode-thicknesses in one diagram. Figure 6 shows this plot of $\eta_{Q(a)}^{\text{max}} - 1$. From figure 6 it can

be seen that the electrode-thickness has a great influence on the efficiency and the greatest sensitivity for the electrode thickness occurs when $l < 0.15$ cm. From figure 6 the electrode thickness $l = 0.18$ cm is obtained for $\eta_{Q(a)}^* = 11.4\%$ and this electrode thickness is the optimal one. With the known $Q(a)$ and l the design porosity can be calculated from equation (3) to give $\epsilon = 0.77$.

Problem II

The solution to problem II for a specified final time can be obtained from a collection of intersections with the final-time hyperbolas and different electrode thickness curves. The intersection coordinates are conveniently plotted in a $Q(a) - l$ diagram. Figure 7 shows $Q(a) - l$ for the final-time 1 min, 100 mA/cm² and 200 mV final polarisation. The smallest amount of active material is obtained as $Q(a) = 2.3$ A.min/cm², which occurs for $l = 0.17$ cm. With equation (3) the design porosity is calculated to be $\epsilon = 0.94$. This porosity value is outside the allowed interval. The nearest interval limit value is 0.85 which has to be chosen as the design porosity. The smallest amount of the active material and the conjugated electrode thickness can be determined from diagram 7 as the intersection between the equations (9) and (10)

$$Q(a) = q_o(1 - \epsilon_{\max}) l \quad (9)$$

$$Q(a) = Q(a)(l, t) \quad (10)$$

Equation (9) is equation (3) implemented with the upper-limit of porosity allowed, $\epsilon_{\max}$ and equation (10) is the relation illustrated in figure 7. Equation (9) is a straight line and the area under this line contains the forbidden solutions to the problem, corresponding to $\epsilon > 0.85$.

The intersection between the equations (9) and (10) gives $l = 0.104$ cm and $Q(a) = 3.24$ A.min/cm². The optimal solution to problem II for 1 minute, 100 mA/cm² and 200 mV final polarisation is $Q^*(a) = 3.24$ A.min/cm², $l = 0.104$ cm and $\epsilon = 0.85$. From the results of problems I and II it can be seen that they do not give identical electrode designs, which of course is the expected result from two different problem formulations. From a general point of view, problem II is more restrictively formulated than problem I. A direct comparison between the functions under consideration give the relations $Q_I^*(a) > Q_{II}^*(a)$ and $\eta_{IQ(a)}^* > \eta_{IIQ(a)}^*$. The relationships show that the higher efficiency gained in problem I is obtained through using a greater amount of active material than is used in problem II which produces a lower efficiency.

Problem III

Figures 8a, b and c show initial time polarisations for sectioned electrodes with the constant electrodespace, $l+d = 0.25$ cm and with the channel-widths $d = 0.05$ and 0.025 (including the collector). The current density for each section is calculated according to equation (7) and for a current-load of 100 mA/cm² on the base-cell. Figure 8a shows for $Q(a) = 5$ A.min/cm² the existence of the best division of the base-space and how this is dependent on the electrode space utilization, $1/(l+d)$. For a space utilization of 90 % ($1/(l+d)=0.90$) $N=3$ is the best division and for 80 % $N=2$ is the best. Commercial high-rate electrodes have a volume utilization around 70-80 %, and with half-channel-widths of about $d = 0.05$ cm and electrode-space $l+d=0.25$ cm. Table 1 shows the current efficiencies for sectioned electrodes in the form of $\eta_{Q(a)}$ to gain materials for a comparison with results from problem I.

Table 1

Table 1 shows that high space utilization combined with the sectioning procedure gives highly utilized electrodes in comparison with base-cell electrodes ($N=1$). The best electrodes are very thin and it can be difficult in practice to manufacture such electrodes and at the same time to maintain the open structure which has been one of the basic considerations in this analysis. The results illustrate the required ideal and suggest the way future work should be directed.

Figure 9 shows some calculated porosities for 100 mA/cm^2 and 200 mV polarisation. The calculated charge-porosity diagram (5) indicates that macro-pore-blockage is not the limiting process at the chosen working conditions. It was reported earlier [1] that low porosity electrodes were macro-pore-blocked at the load-level of 100 mA/cm^2 . The final polarisation considered here is 200 mV and the one reported earlier was 500 mV, which explains the differences in the limiting processes.

CONCLUSION

The calculations presented here, although limited in scope, demonstrate the importance of proper formulation of optimization problems in electrode design. The analysis presented here could be extended to new and old active materials to obtain a range ensemble of efficiently characterised active materials. This ensemble would then be suitable to use in the efforts to determine the ultimate performance for porous electrodes.

Symbols

d	half electrolyte-channel width, cm
i	current density, A/cm ²
I	current load, A
K	constant defined by equation (7), A.min
l	half electrode-thickness, cm
N	electrode space division number
q	volume capacity with porosity included, A.min/cm ³
q ₀	theoretical volume capacity, A.min/cm ³
Q(a)	capacity whithin the system volume, projected on the electrode surface perpendicular to the channel current, A.min/cm ²
Q(b)	capacity whithin the system volume, projected on the electrode base area, A.min/cm ²
ε	porosity
η	efficiency
*	optimal

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Table 1

The efficiency $\eta_{Q(a)}$ for 100 mA/cm² and 200 mV final polarisation. The system volume $(l+d) \cdot l^2 = 0.25 \text{ cm}^3$ and the spalt widths 0.05 and 0.025 cm.

N = 1 base-cell

division number N	volume utilization $\frac{1}{l+d}$	capacity A.min/cm ² Q(a)	efficiency per cent $\eta_{Q(a)}$	thickness cm l	porosity ϵ
4	0.90	3.0	84.8	0.0375	0.628
4	0.90	2.0	83.0	0.0375	0.750
3	0.90	3.0	63.4	0.0583	0.757
3	0.90	2.0	58.0	0.0583	0.839
3	0.80	3.0	50.6	0.0333	0.575
3	0.80	2.0	46.0	0.0333	0.718
2	0.90	5.0	36.8	0.10	0.760
2	0.80	3	30.0	0.075	0.812
1	0.80	5.	8.8	0.20	0.880

Figure captions

Figure 1

Calculated initial time over-potentials shown as functions of the electrode-thickness l for a current load of 100 mA/cm^2 . The parameters are the values of porosity for charged electrodes.

Figure 2

The base-electrode with the assumed system-volume. Surface (a) is the electrode cross-section area perpendicular to the electrode-current direction. Surface (b) is the bottom-projection of one symmetrical part of the electrode with one half of the electrolyte-channel included.

Figure 3

The general relation between current-efficiency $\eta_{Q(a)}$ and the built-in capacity $Q(a)$. The dotted line is the tie-line for maximum points on the $\eta_{Q(a)} - Q(a)$ curves.

Figure 4

The electrode volume utilization ratio $l/(l+d)$ as a function of available space, $l+d$. The different curves represent different values of d , whose value can be obtained from $l/(l+d)=0$ co-ordinates.

Figure 5

Current-efficiency, $\eta_{Q(a)} - Q(a)$, curves for 100 mA/cm^2 and 200 mV final polarisation. The dotted tie-line connects different maximum points from the different parameterised electrode-thicknesses curves, 0.8, 1., 1.5 and 2 mm respectively. The parameters on the hyperbolas are given for various final times in minutes.

Figure 6

The curve showing conjugated pairs of points for maximum current efficiency and electrode-thickness in connection with figure 5.

Figure 7

The curve showing sub-optimal solutions $Q(a) - 1$ to problem II for 1 minute final time, 100 mA/cm^2 and 200 mV final polarisation. The areas within the given porosity inequalities violate the assumed porosity restriction and represent forbidden regions of solutions.

Figure 8a, b, c

Initial polarisations for sectionized electrodes for a load of 100 mA/cm^2 to the base-volume. The symbols are, $\square$ for 90 % electrode utilization of the system volume and $\circ$ for 80 % utilization respectively ($1/(1+d)$, 0.90 respectively 0.80). The number on the symbols corresponds to the cell-space division numbers of the base-electrode volume. The separate figures are for different capacities $Q(a) \text{ A.min/cm}^2$.

Figure 9

A charge-porosity diagram showing calculated final porosities in the pore-mouth region for two different electrode-thicknesses. The diagram is constructed for a load of 100 mA/cm^2 and a 200 mV final polarisation. The initial states were on the full-charged line. (The diagram is presented in reference (5)).

Fig. 1

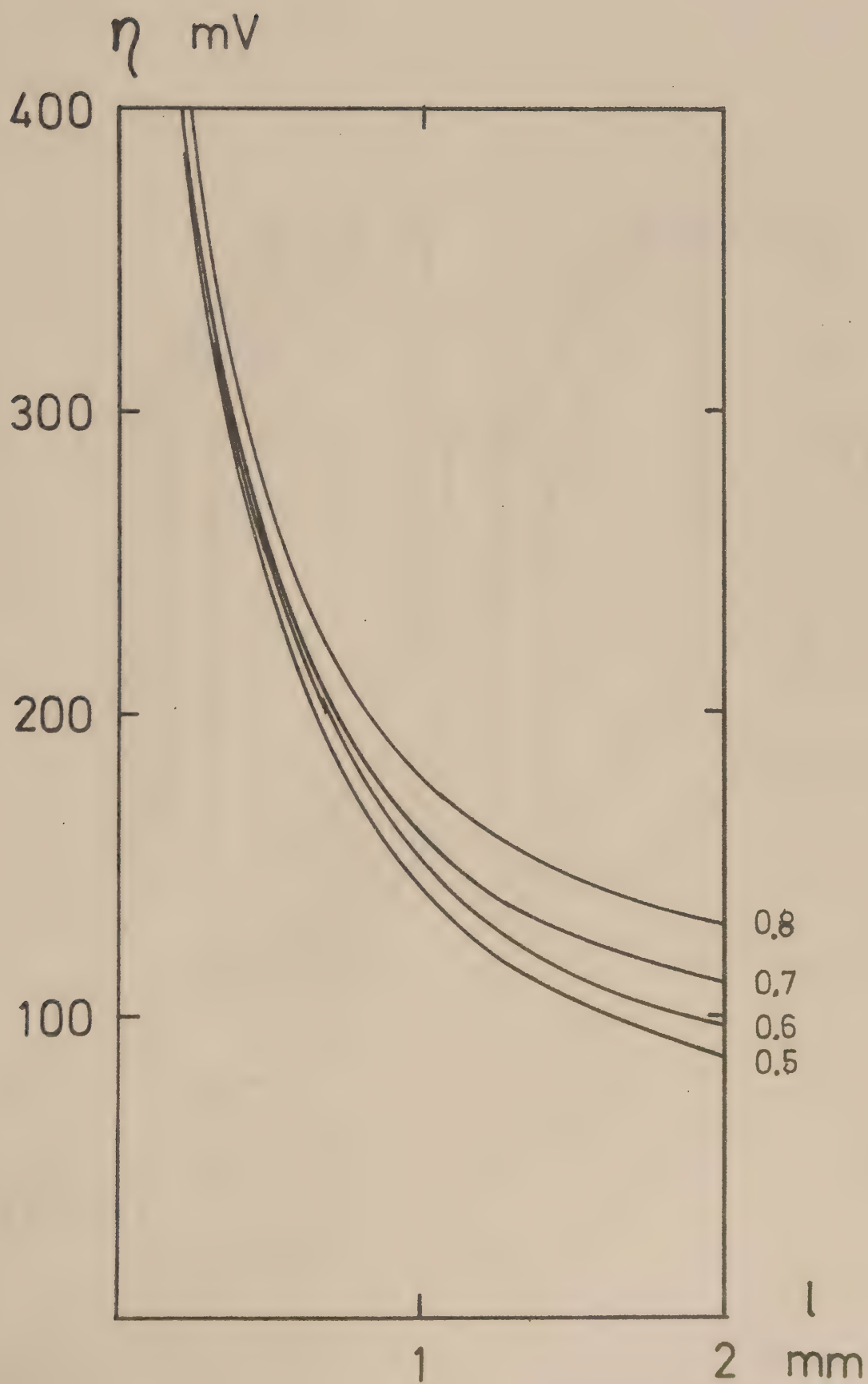


Fig. 2

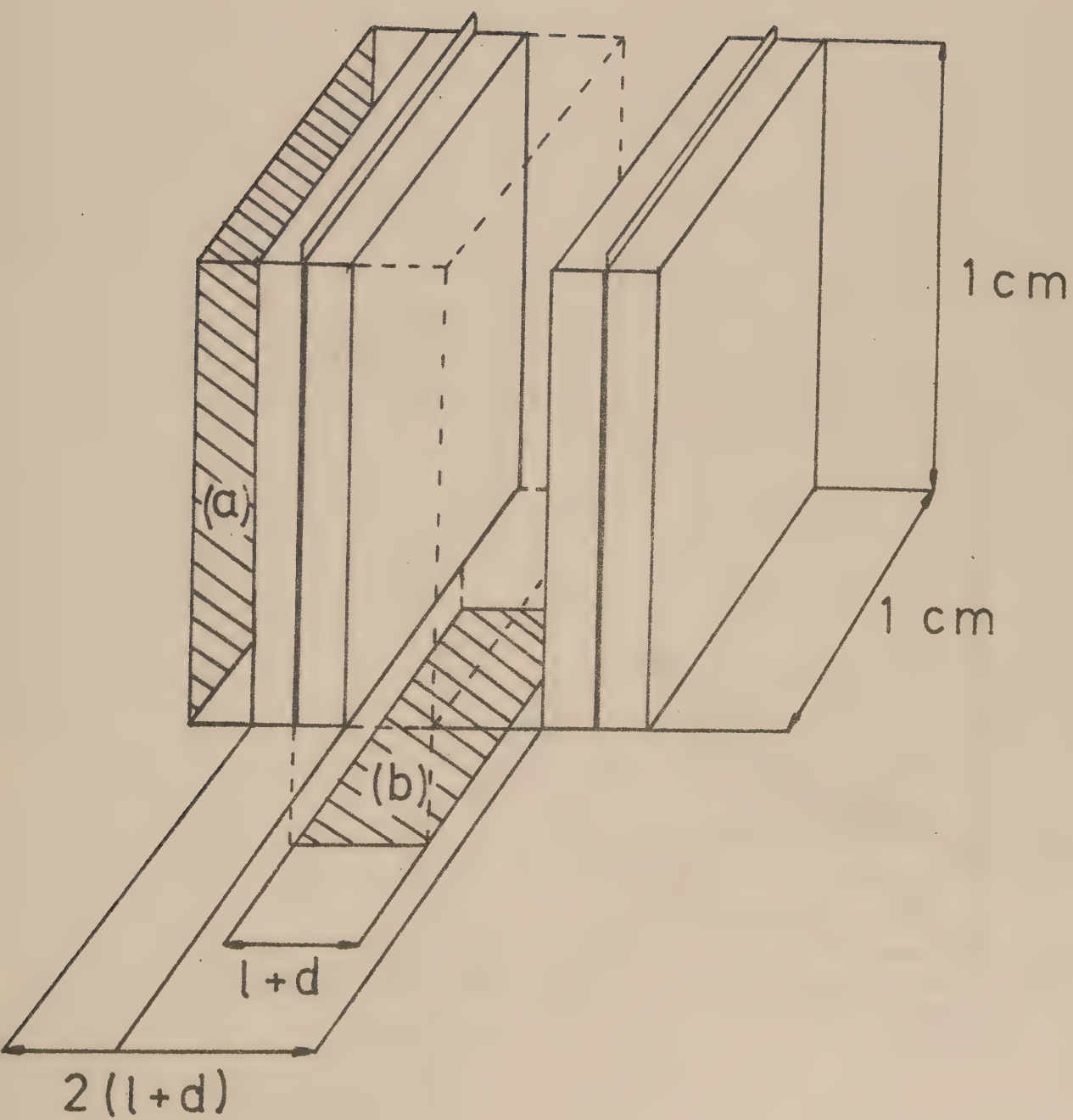
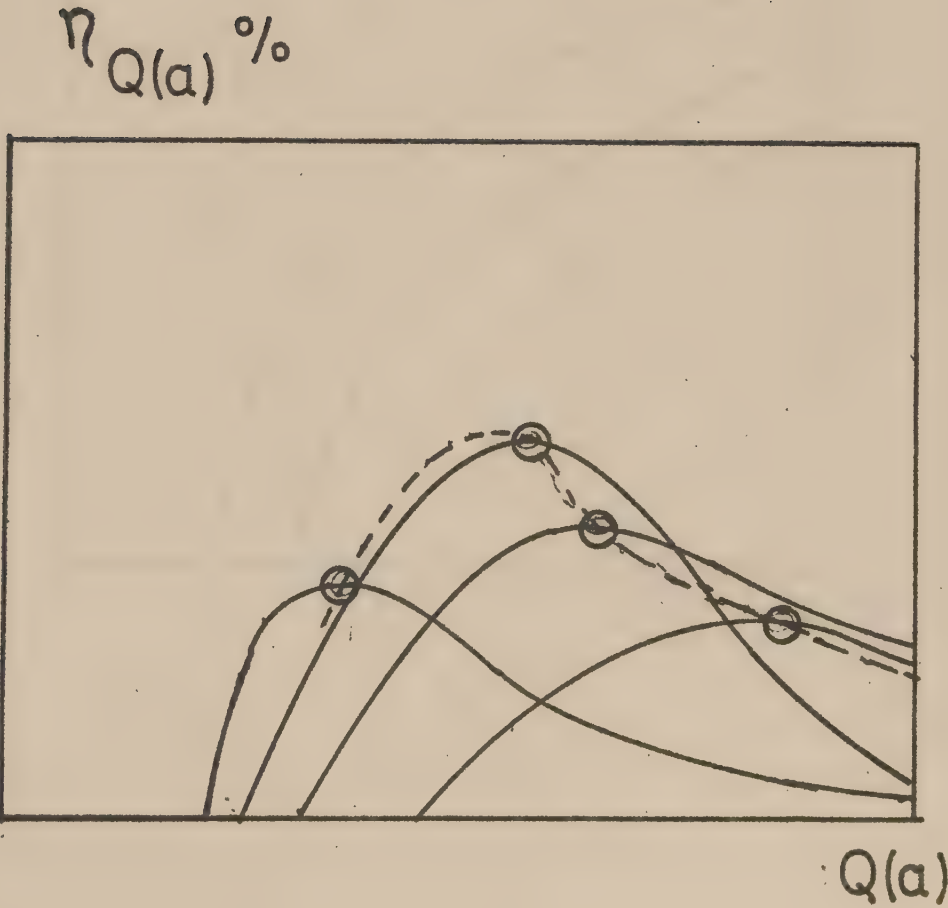
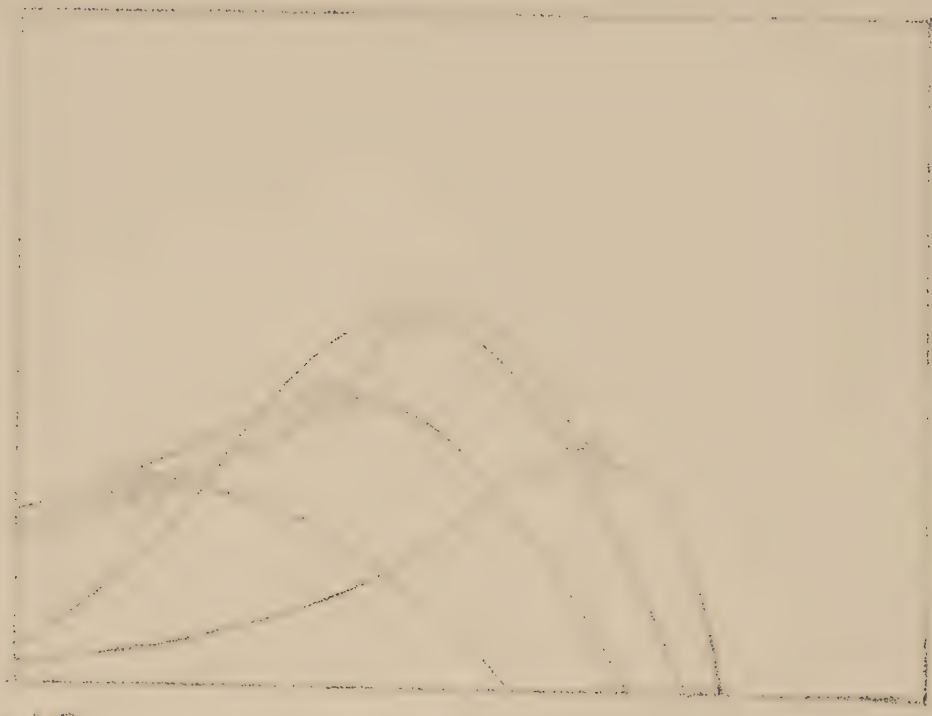


Fig. 3



17. 10. 1957



(D)

Fig. 4

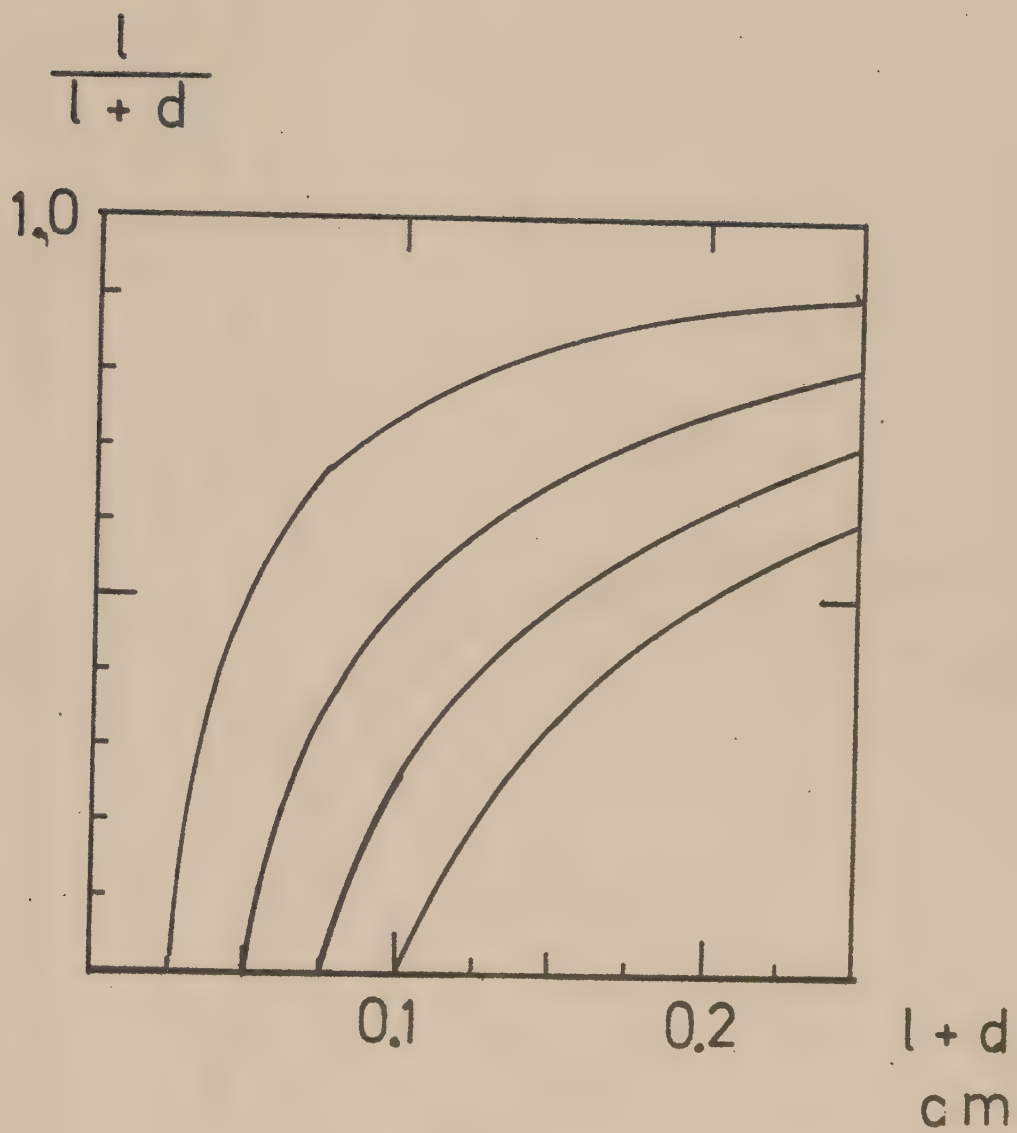


Fig. 5.

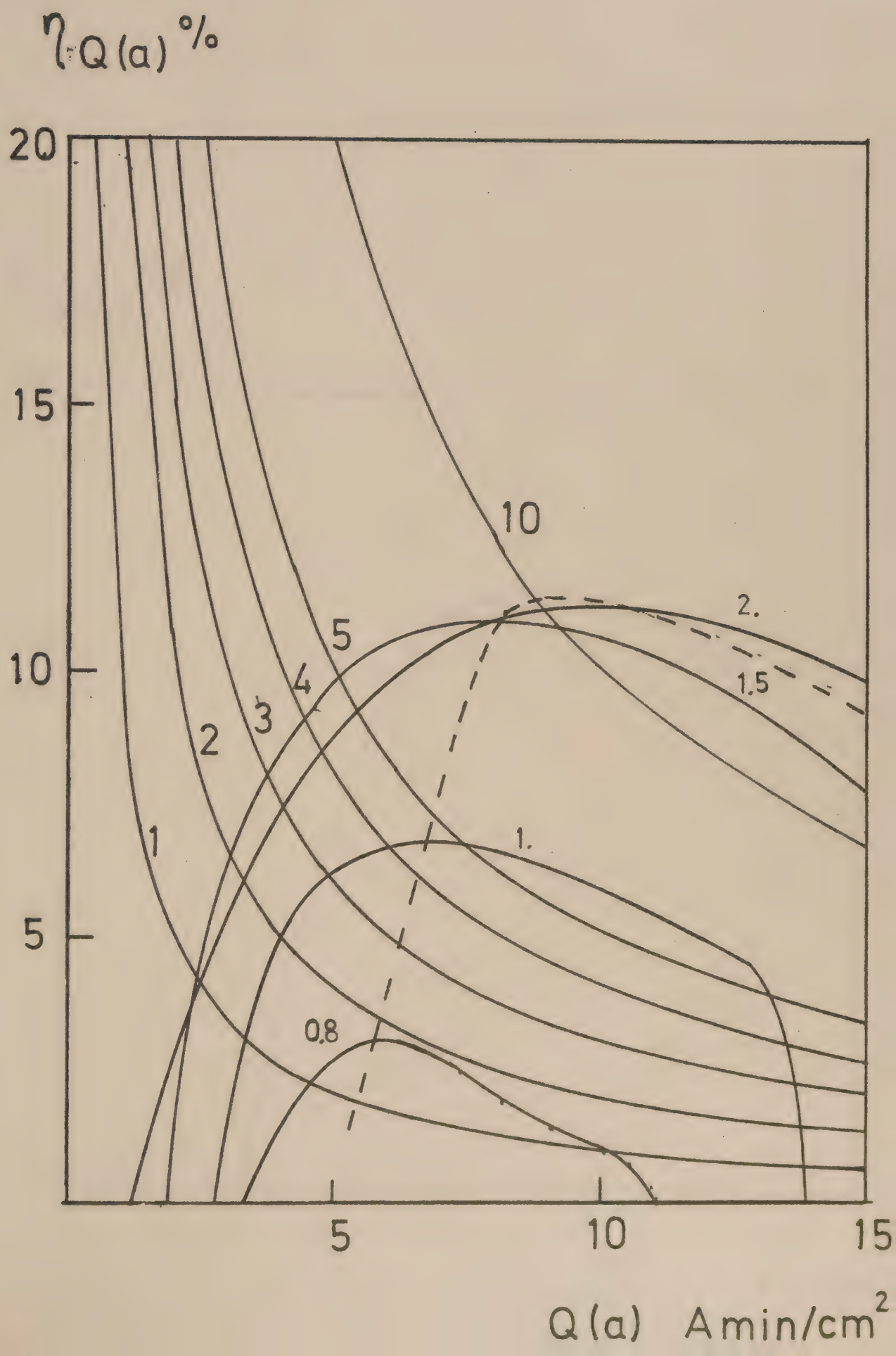


Fig.6

$\eta_{Q(a)} \%$

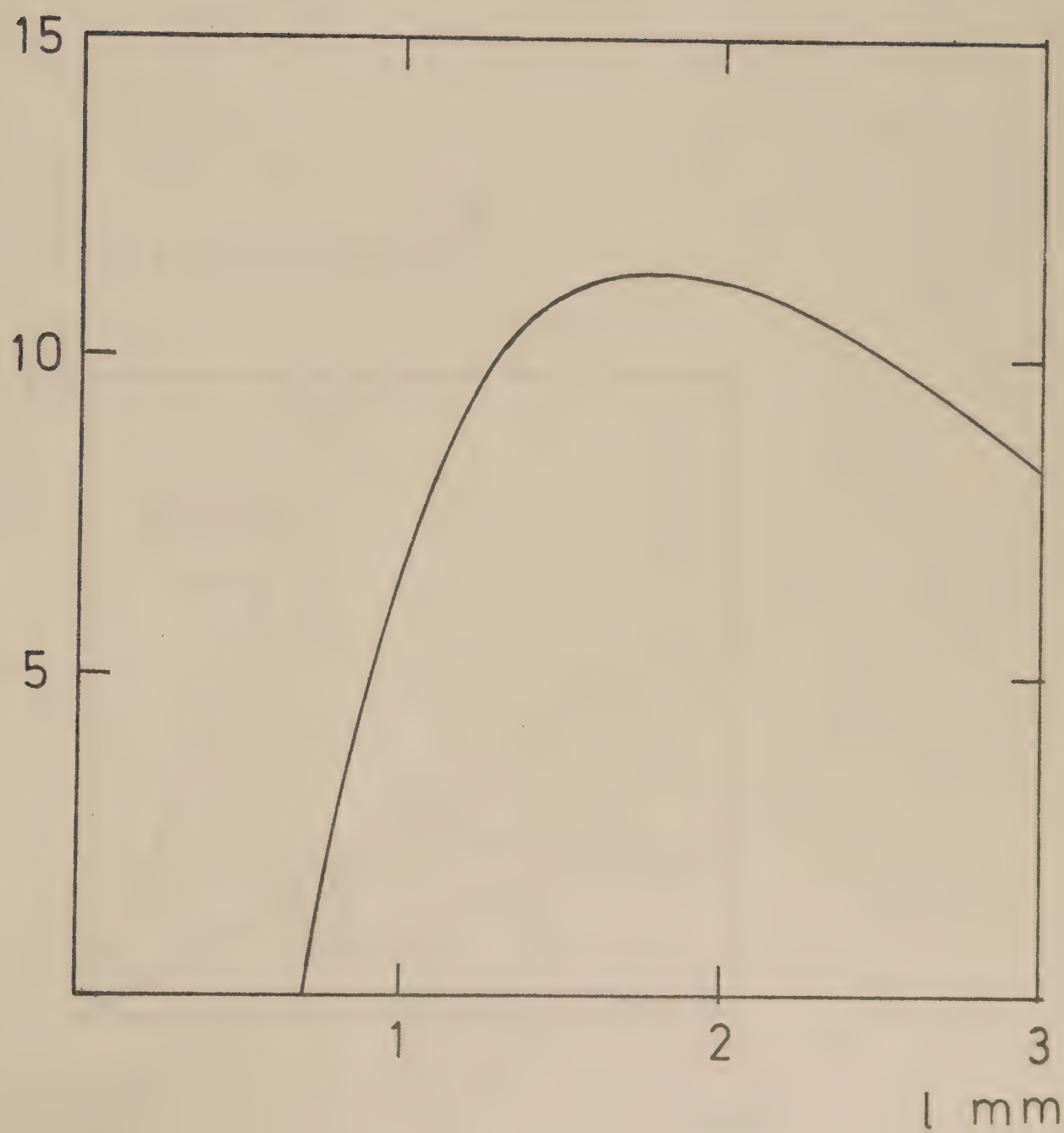


Fig. 7

$Q(a)$ A_{min}/cm^2

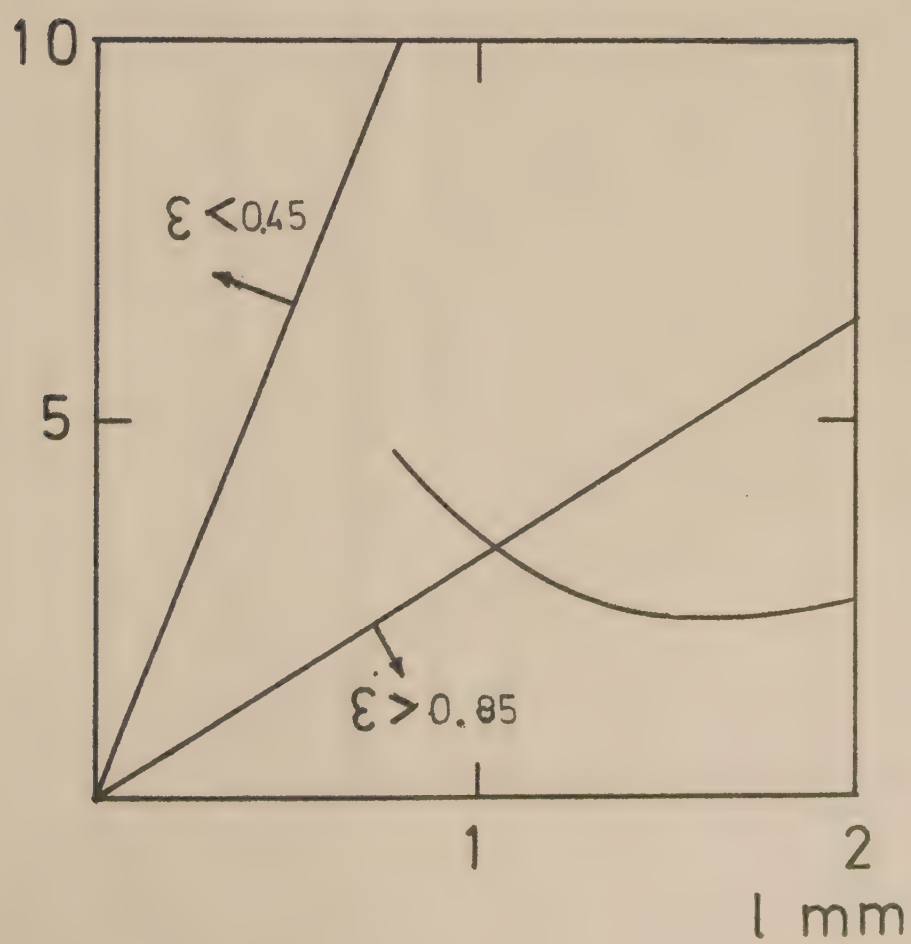


Fig. 8 a

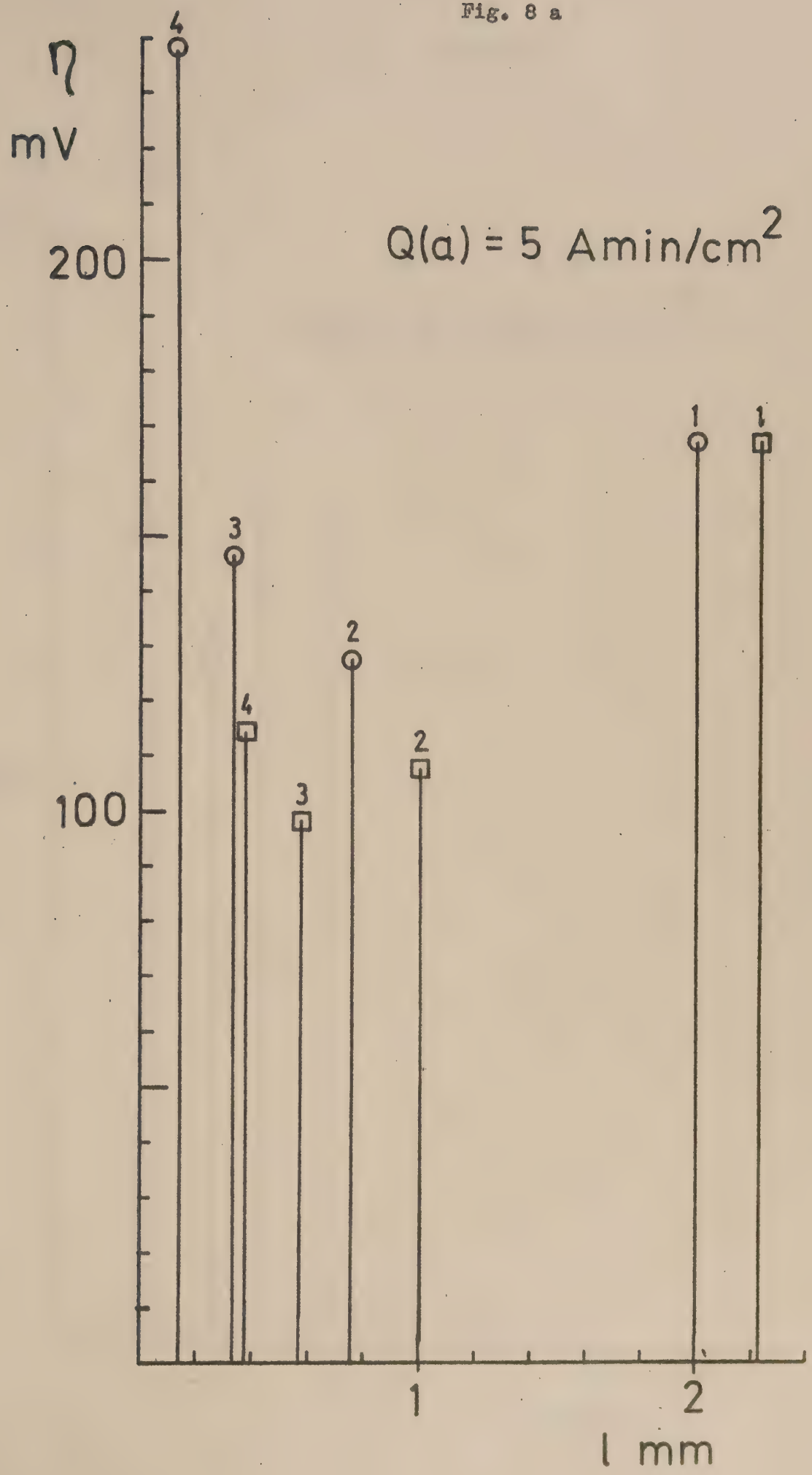
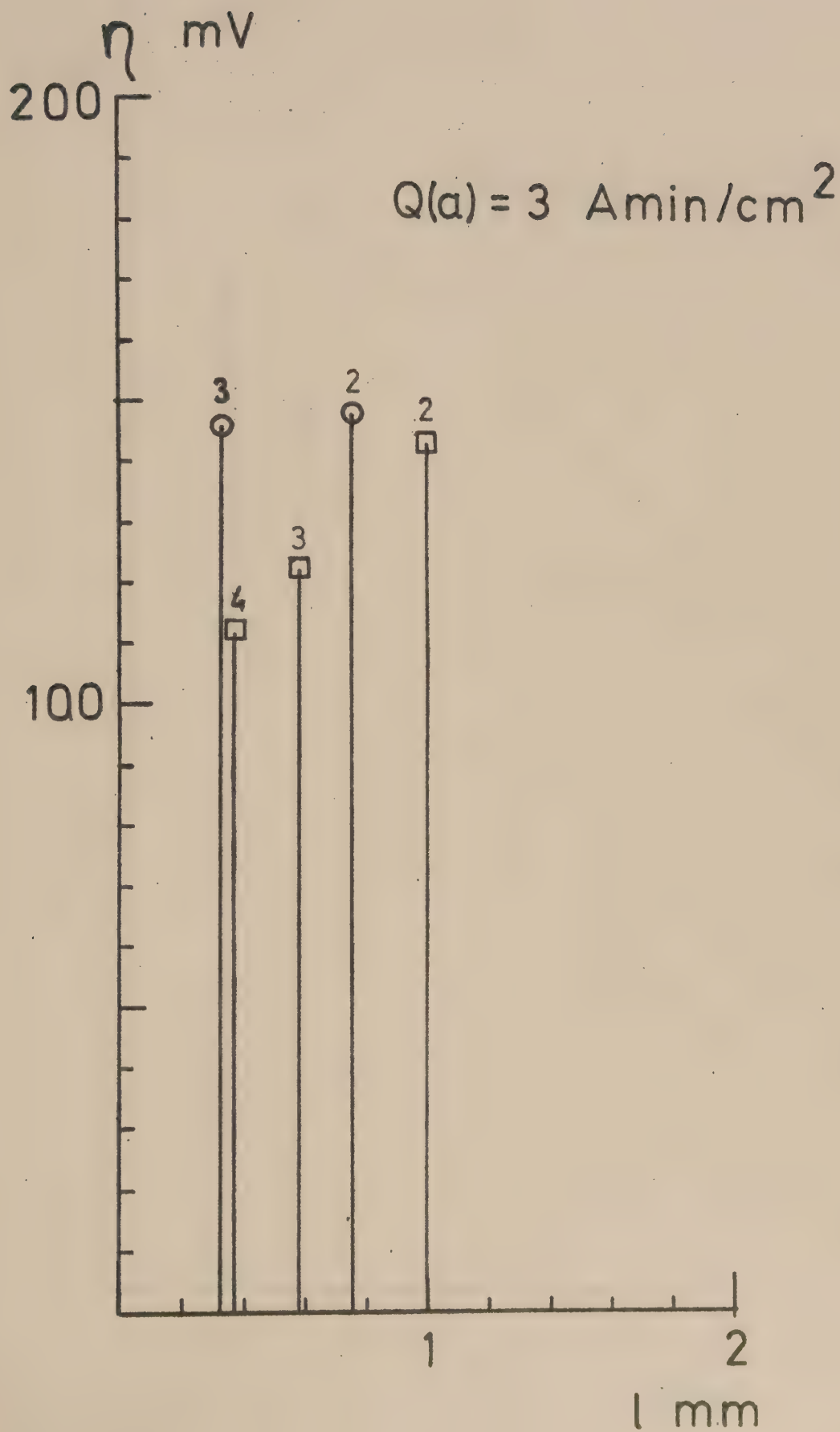


Fig. 8 b



Spectrum A E (10)

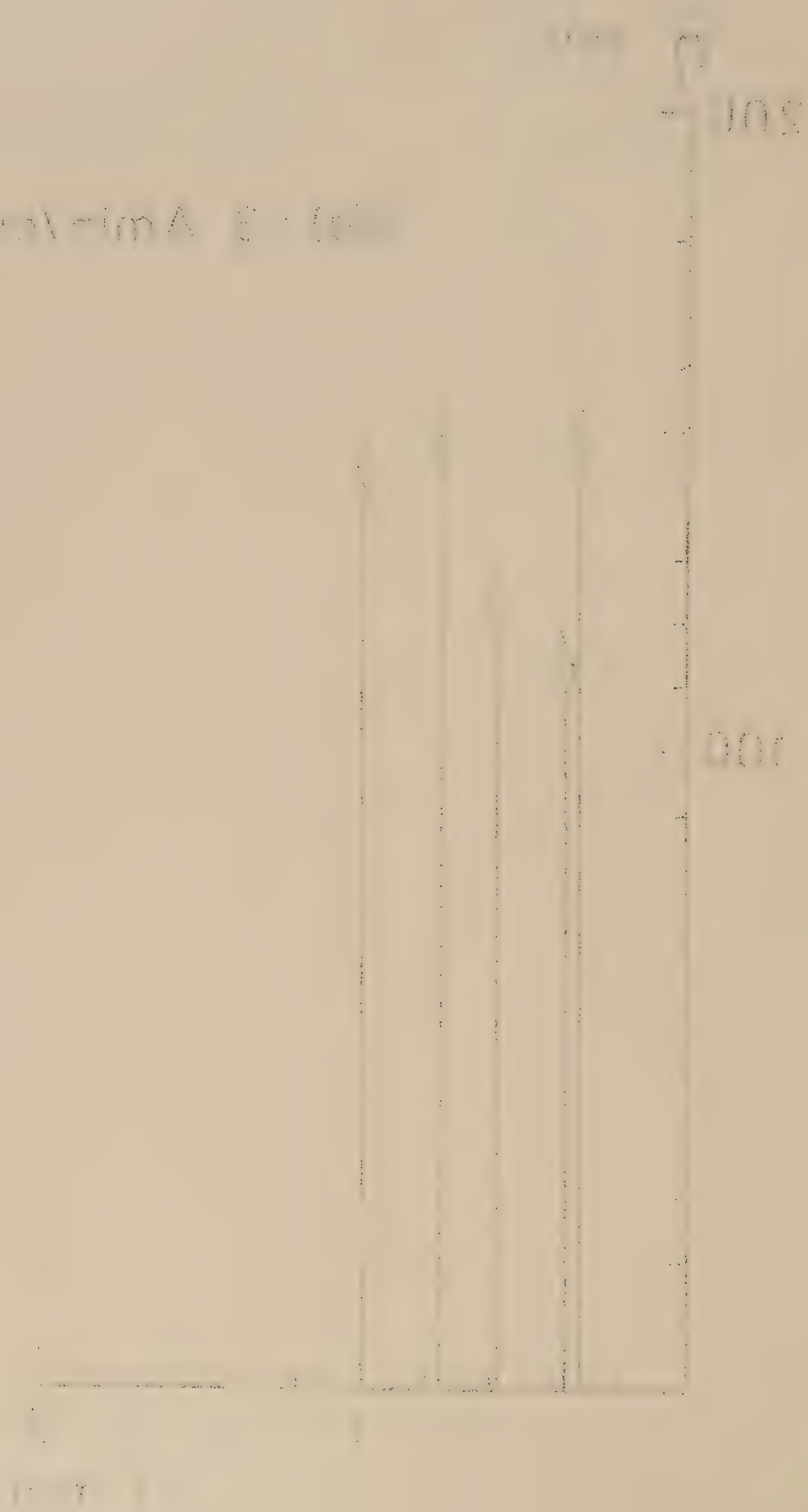


Fig. 8 c

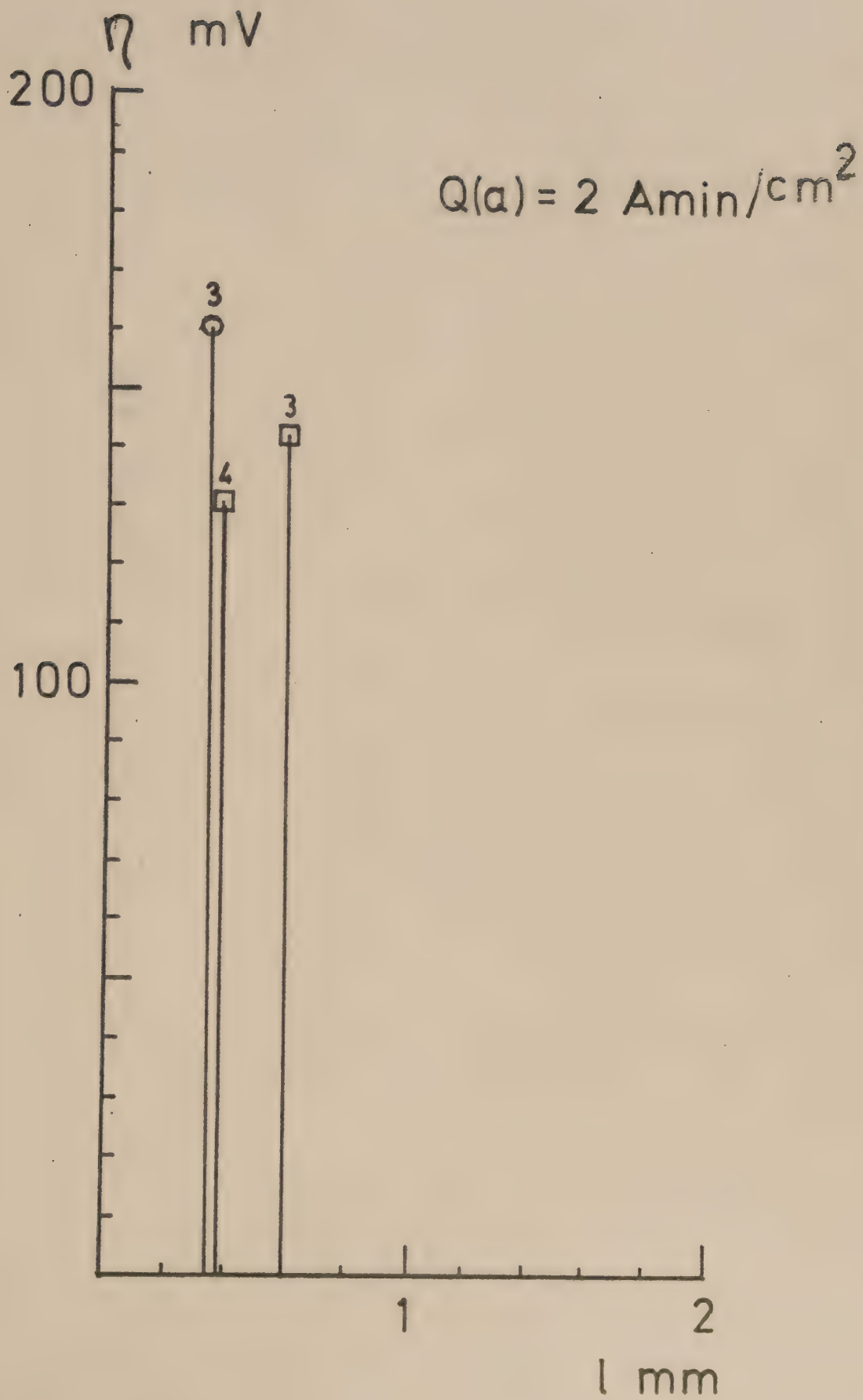


Fig. 9

